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α,ω-Di(glycerol carbonate) Telechelic Polyesters and Polyolefins as Precursors to PolyHydroxyUrethanes: an Isocyanate-free approach

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Abstract

α,ω-Di(glycerol carbonate) telechelic poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG), poly(ester ether) (PEE), and poly(butadiene) (PBD) have been synthesized upon chemical modification of the corresponding α,ω-dihydroxy telechelic polymers (PPG-OH_2, PEG-OH_2, PEE-OH_2 and PBD-OH_2, respectively). Tosylation of the polymer diols with 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) afforded, in high yields, the desired PPG, PEG, PEE and PBD end-capped at both termini with five-membered ring cyclic glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, GC). The GC-functionalization of the polymers at both chain-ends has been confirmed by NMR (^{1}H, ^{13}C, 1D and 2D) and FTIR spectroscopies. Using PPG-GC_2 to demonstrate the concept, the corresponding polyhydroxyurethanes (PHUs/non-isocyanate polyurethanes (NIPUs)) have been subsequently prepared following a non-isocyanate method, upon ring-opening catalyst-free polyaddition of the PPG-GC_2 with JEFFAMINEs (M_n = 230-2000 g.mol^{-1}). The effect of various additives introduced during the polyaddition reaction has been studied at different temperatures. In particular, addition of LiBr (5 mol%) to the reaction medium was found to slightly promote the cyclocarbonate/amine reaction. The polymerization process was supported by FTIR and by SEC analyses.

Keywords

Diol, Glycerol carbonate, telechelic polymers, hydroxy telechelic polymers, non-isocyanate polyurethane (NIPU), poly(hydroxy urethane) (PHU), poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), poly(butadiene) (PBD), polyester

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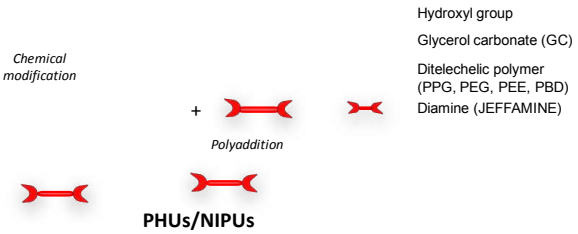
Synthesis of α,ω-di(glycerol carbonate) telechelic polyesters, polyethers and polydienes as precursors to polyhydroxyurethanes in a catalyst-free, isocyanate-free procedure.



Introduction

With a global market reaching 14 million tons in 2011, polyurethanes (PUs) are attracting much attention both in industry and in academia. Indeed PUs are used in a wide range of applications as commodity or specialty polymer materials, including adhesives, coatings, sealants, foams, thermoplastics, thermorigids, elastomers, or implantable biomedical devices.[1] PUs featuring pendant functional and reactive hydroxy groups, namely polyhydroxyurethanes (PHUs), have also become increasingly investigated for their appealing mechanical and degradation properties.[2] PHUs exhibit, in comparison to PUs, greater thermal stability (degradation temperature of a urethane unit *ca*. 230 °C) as the result of the absence of biuret (degradation temperature *ca*. 150 °C) or allophanate (degradation temperature *ca*. 120 °C) groups. Also, the intermolecular and intramolecular hydrogen bondings between the hydroxyl groups and the β-carbonyl oxygens within urethane repeating units render PHUs more resistant to organic solvents. In addition, the hydroxyl groups provide greater hydrophilicity and decreased crystallinity, thus making the polymer less vulnerable to environmental degradation. Besides, in regard of general "green considerations", such PHUs are harmless in terms of toxicity. Finally, chemical modification of the pendant OH groups further provides several opportunities.[1,2]

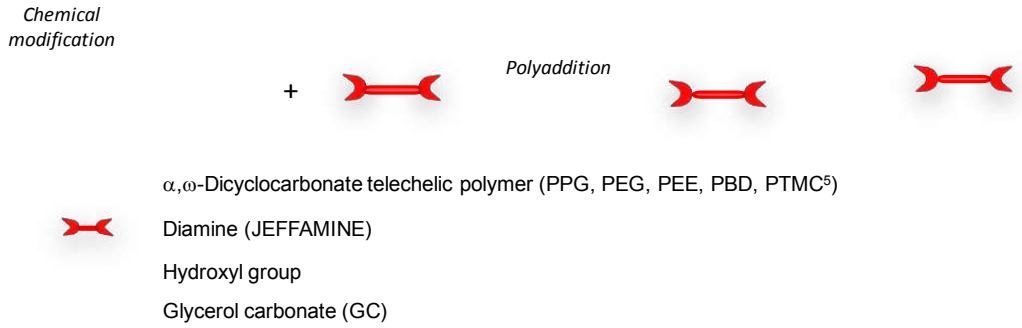
The common method for the production of PUs involves the reaction of isocyanates with diols/polyols catalyzed by a tin compound (most commonly, dibutyl tin laurate (DBTL)). In this process, the use of hazardous isocyanates and phosgene has raised severe toxicity and environmental issues.[1] However, within the recent scientific eagerness towards biofriendly PUs, current attention is being focused on the development of non-isocyanate polyurethanes (NIPUs).[2,3] Sustainable routes to NIPUs essentially revolve around the valorization of various renewable natural oil polyols (referred to as NOPs) derived from plants. Extensive work aims at chemically modifying vegetable oils (triglycerides, i.e. soybean, sunflower, palm, linseed

oils…) so as to establish a chemical platform as non-petrochemical feedstock for the synthesis of NIPUs.[4] This approach certainly presents numerous advantages among which the major one is the accessibility to renewable triglycerides which remain the cheapest and most abundant biological sources available. However, the one significant limitation of these NIPU precursors remains their molar mass which cannot be fine-tuned – as it is essentially dictated by the natural oil itself – which restrains their range of properties and therefore of applications.

Within our ongoing studies on NIPUs derived from synthetic polymers, we are developing such polymer materials with a tunable/controlled soft segment molar mass.[5,6] Our general strategy involves the synthesis of α,ω-dicyclocarbonate end-functionalized pre-polymers which are subsequently reacted with a diamine in a polyaddition reaction to provide PHUs in an isocyanate-free process (Scheme 1). Following the pioneering studies of, in particular Endo, on the ring-opening of five-, six- or seven-membered ring cyclic carbonates by amines affording PHUs/NIPUs of molar mass in the range of M_n = 20,000–30,000 g.mol^{-1},[7,8] there is currently a reemergence of this "cyclic carbonate/amine" route. One of our approaches consists in the direct synthesis of five-membered ring cyclic glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, GC) end-capped polyolefins, from the ring-opening metathesis polymerization (ROMP) using GC derivatives as chain transfer agents.[6] In particular, acryloyl-GC smoothly enabled the preparation of well-defined α,ω-di(glycerol carbonate) telechelic poly(cyclooctene) with $M_{n,NMR}$ up to 49,200 g.mol^{-1} and $Đ_M$ = 1.54. Besides this direct route, our earlier achievement enabled the synthesis of poly(trimethylene carbonate) (PTMC) end-capped at both termini by GC (PTMC-GC_2), obtained upon chemical modification of the analogous α,ω-dihydroxy telechelic PTMC (PTMC-OH_2) – itself prepared by ring-opening polymerization of the corresponding trimethylene carbonate monomer derived from glycerol.[5,9,10] The corresponding high molar mass ($M_{n,SEC}$ = 68,100 g.mol^{-1}; $Đ_M$

= 1.20) poly(TMC hydroxyurethane) was next prepared upon ring-opening polyaddition with 1,6-hexanediamine. We currently aim at extending this latter original route to NIPUs, using other dihydroxy- and subsequently dicyclocarbonate-telechelic pre-polymers, as well as other diamines such as the Jeffamines, ultimately offering NIPUs/PHUs featuring various properties. (Scheme 1). To our knowledge, besides these two examples,[5,6] dicyclocarbonate telechelic polymers remain rare. Another objective of our work is to valorize GC a cheap bio-resourced alcohol obtained from glycerol, a side-product formed during the production of biodiesel and available in large quantities, as well as to promote a "greener" route. Indeed, GC is a versatile building block, nowadays driving many investigations aimed at its valorization, including in the polymer field.[11] Note that NIPUs have otherwise been prepared from a biscarbonate urethane featuring a glycerol carbonate moiety at each extremity and a diamine.[12]

Also, one major flaw of the glycerol carbonate/amine reaction that prevents large-scale industrial production is the high stability of the five-membered ring which considerably slows down the polymerization. Catalysts or additives are thus highly desirable to accelerate this polyaddition, although their exact operating mode remains unclear. Besides tin-based compounds (such as dibutyltinlaurate, DBTL), the use of salts that may enhance the nucleophilic addition to oxacyclic compounds or of simple bases have been reported. Also, weak yet oxophilic Lewis acids are expected to coordinate the carbonyl group of GC, possibly weakening/activating it by increasing its electrophilicity.[7c,g,i,l,8] In particular, LiBr, and to a lesser extent KO^{t}Bu or TBD have been shown as the most potent additives. Finally, the other main challenge to overcome for the carbonate/amine route to be competitive with the traditional isocyanate-based preparation of PUs, is to access high molar mass polymers.

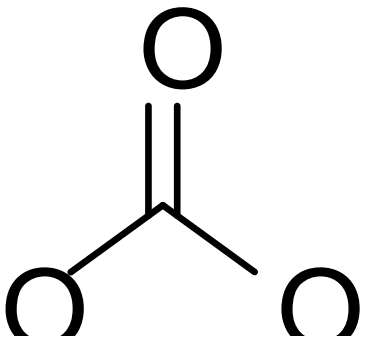


Scheme 1. Concept for the preparation of NIPUs/PHUs from the carbonate/amine reaction.

In the present contribution, we report the synthesis of α,ω-di(glycerol carbonate) telechelic poly(propylene glycol) (PPG-GC_2), poly(ethylene glycol) (PEG-GC_2), poly(ester ether) (PEE-GC_2), and poly(butadiene) (PBD-GC_2), upon reaction of the corresponding α,ω-dihydroxy telechelic polymers (PPG-OH_2, PEG-OH_2, PEE-OH_2 and PBD-OH_2, respectively; Scheme 2) with glycerol carbonate tosylate (GC-OTs). As a conceptual demonstration, the PPG thus end-capped at both termini with GC were subsequently reacted with JEFFAMINEs as diamines of different molar mass, at different temperatures and over different reaction times, thereby affording upon ring-opening polyaddition, the desired PHUs/NIPUs (Scheme 3). Our present investigations also address the efficiency of several additives to promote the carbonate/amine reaction.

Scheme 2. α,ω-Dihydroxy- and α,ω-di(glycerol carbonate) telechelic pre-polymers used towards the synthesis of PHUs/NIPUs.

Step 1:
Synthesis of the GC



Scheme 3. Synthesis of PPGHU prepared from PPG-OH_2 via PPG-GC_2 (for the sake of clarity, all possible regioisomers of PPGHU obtained upon ring-opening of the cyclocarbonate ring are not represented).

Experimental section

Methods and Materials

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, GC) was purchased from ABCR chemicals and used as received. 4-Chloromethyl-1,3-dioxolan-2-one was synthesized according to the reported literature procedure.[13] Glycerol carbonate tosylate (GC-OTs) was synthesized in 65% yield from GC through deprotonation with NaH and subsequent tosylation with TsCl (Scheme S1).[14] NMR spectra are in agreement with reported data (Figures S1 and S2 for ^{1}H and ^{13}C NMR spectra, respectively).[15] α,ω-Dihydroxy telechelic poly(propyleneglycol) (VORANOL Polyol, Bostik, PPG-OH_2), poly(ethyleneglycol) (Bostik, PEG-OH_2), poly(ester ether) (REALKYD XTR 10410, Cray Valley, PEE-OH_2; a polymer produced from the polycondensation of adipic acid and diethyleneglycol), and poly(butadiene) (POLYBD R45 HTLO, Cray Valley, PBD-OH_2) featuring various molar mass values (Tables 1, S1−S3) were used as received. JEFFAMINEs (EDR 176, Huntsman; JA_{230}, JA_{400}, JA_{2000}; M_n = 230, 400, and 2000 g.mol^{-1}, respectively) were used as received.

Instrumentation and measurements

^{1}H (500 MHz) and ^{13}C{^{1}H} (125 MHz) NMR spectra were recorded on a Brüker Avance AM 500 spectrometer at 25 °C in $CDCl_3$ using a relaxation delay of 3 s to enable quantitative analysis. ^{1}H and ^{13}C NMR spectra were referenced internally relative to $SiMe_4$ (δ 0 ppm) using the residual solvent resonances.

Average molar mass ($M_{n,SEC}$) and dispersity ($Đ_M = M_w / M_n$) values of the polymers were determined by size-exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL.min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μm MIXED-C 300 × 7.5 mm columns. The polymer samples were dissolved in THF (2 mg.mL^{-1}). Average molar mass and dispersity values of high molar mass PHUs were determined by SEC in DMF with LiBr (1 g.L^{-1}) at

60 °C (flow rate = 0.8 mL.min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μm MIXED-D 300 × 7.5 mm columns. The polymer samples were dissolved in DMF (2 mg.mL^{-1}). All elution curves were calibrated with eleven monodisperse polystyrene standards (range of 300 to 380,000 g·mol^{-1}), and $M_{n,SEC}$ values of the polymers were uncorrected for the potential difference in hydrodynamic radius vs. polystyrene.

The molar mass of short-chain PPG samples was determined by ^{1}H NMR analysis in $CDCl_3$ from the relative intensities of the signals of the PPG main-chain methyl hydrogens (C*H*$_3$CH, δ 1.11 ppm) and those of the chain-end methylene hydrogens of GC (–CHOC(O)OC*H*$_2$–, δ 2.82, 2.64 ppm) signals.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF) mass spectra were recorded on an AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N_2 laser source (337 nm, 4 ns pulse width) and time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and an accelerating voltage of 20 kV. The polymer sample was dissolved in THF (HPLC grade, 10 mg.mL^{-1}). A saturated solution of α-cyano-4-hydroxycinnamic acid (Aldrich, 99%; 10 mg.mL^{-1}) in acetonitrile (HPLC grade) was prepared. This latter solution was then mixed in a 3:2 volume ratio with a 0.1% trifluoroacetic acid (TFA) solution in water. Both solutions were deposited sequentially on the sample target and then air-dried. Bruker Care Peptide Calibration and Protein Calibration 1 Standards were used for external calibration.

FTIR spectra of the polymers were acquired (32 scans) with a resolution of 4 cm^{-1} on a Shimadzu IRAffinity-1 equipped with an ATR.

Synthesis of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs). NaH (1.5 g, 65 mmol) was slowly added to a solution of glycerol carbonate (7.0 g, 59 mmol) in THF (80 mL) at 0 °C. The resulting suspension was stirred at 0 °C for 20 min, then warmed to room temperature

and next stirred over 40 min. A solution of tosyl chloride (11.3 g, 59 mmol) in THF (50 mL) was then added, and the resulting white suspension was stirred at room temperature over 48 h. Then, a few drops of a saturated aqueous solution of NH_4Cl were added at 0 °C. The product was next extracted with toluene (3 × 50 mL); the organic fraction was dried over Na_2SO_4 and the solvent distilled off by rotary evaporation. The recovered material was purified by silica gel chromatography (pentane:ethyl acetate, 1:4 as eluent) to afford 4-tosylmethyl-1,3-dioxolan-2-one as a white powder (10.5 g, 65%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.45 (3H, s, Ph-*CH*$_3$), 4.20-4.55 (4H, m, C*H*$_2$-CH-and C*H*$_2$OSO$_2$), 4.86 (1H, m, CH$_2$-C*H*-OCOO), 7.48 (2H, d, *o*-C_6H_5), 7.78 (2H, d, *J* = 9 Hz, *m*-C_6H_5) (Figures S1). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 21.7 (*C*H$_3$), 65.8, 68.9, 44.5 (*C*H$_2$-GC), 73.2, 48.9 (*C*H-GC), 127.9, 130.2, 131.8, 145.8 (Ar-C), 154.3 (O=*C*OO) (Figure S2).

Functionalization of PPG-OH$_2$ with GC-OTs. NaH (0.150 g, 6.5 mmol) was slowly added to a solution of PPG-OH$_2$ (Figure S4 and Table 1; 1.00 g, 2.5 mmol) in THF (100 mL) at 0 °C. The resulting suspension was stirred at 0 °C over 20 min, then warmed to room temperature and next stirred over 60 min. GC-OTs (1.40 g, 5.1 mmol) was then added and the resulting white suspension was stirred at room temperature for 48 h. A few drops of a saturated aqueous solution of NH_4Cl were then added at 0 °C. The product was extracted with toluene (3 × 50 mL), the organic fraction was dried over Na_2SO_4 and the solvent distilled off. The recovered material was next dissolved in ether (50 mL) and the precipitate was removed by filtration. The filtrate was dried under vacuum to remove the solvent. A clear light-yellow oil was thus recovered (0.90 g, 90%). The final polymer was characterized by 1D and 2D NMR and FTIR, evidencing the almost quantitative functionalization (96%) of PPG-OH$_2$, and by SEC analysis (Table 1 and Figures 1, 2, 3 and Figures S5,S6).

Functionalization of PEG-OH$_2$ with GC-OTs. NaH (0.240 g, 10.0 mmol) was slowly added to a solution of PEG-OH$_2$ (Figure S7; 2.00 g, 5.0 mmol) in THF (30 mL) at 0 °C. The

resulting suspension was stirred at 0 °C over 20 min, then slowly warmed at room temperature and next stirred over 90 min in order to ensure complete deprotonation. GC-OTs (2.85 g, 10.5 mmol) was next added and the resulting white suspension was stirred at room temperature for 48 h. The desired product was recovered following the same procedure as described above for the isolation of PPG-GC_2. A colorless oil was thus recovered (1.62 g, 81%). The final polymer was characterized by 1D and 2D NMR, and FTIR analyses, evidencing the almost quantitative functionalization (99 %) of PEG-OH_2, and by SEC analysis (Figures S8, S9, S10, S11).

Functionalization of PEE-OH_2 with GC-OTs. NaH (0.120 g, 5.1 mmol) was added to a solution of α,ω-dihydroxy telechelic poly(ester ether) (PEE-OH_2, M_n = 1,000 g.mol^{-1}; Figures S12, S13 and Table S2; 2.30 g, 2.3 mmol) in THF (30 mL) at 0 °C. The resulting suspension was stirred at room temperature over 2 h. GC-OTs (1.27 g, 4.65 mmol) was then added and the resulting white suspension was stirred at room temperature for 48 h. The desired product was recovered following the same procedure as described above for the isolation of PPG-GC_2. A clear light oil was thus recovered (2.07 g, 90%). The final polymer was characterized by 1D and 2D NMR, FTIR and MALDI-ToF MS evidencing the almost quantitative functionalization (98%) of the PEE-OH_2, and by SEC analysis (Table S2 and Figures S14, S15, S16, S17, S18,S19).

Functionalization of PBD-OH_2 with GC-OTs. NaH (0.080 g, 3.3 mmol) was slowly added to a solution of PBD-OH_2 (2.90 g, 0.85 mmol; Figure S20) in THF (40 mL) at 0 °C. The resulting suspension was stirred at room temperature 3 h in order to ensure complete deprotonation. GC-OTs (0.50 g, 1.8 mmol) was next added and the resulting white suspension was stirred at room temperature over 6 days. The desired product was recovered following the same procedure as described above for the isolation of PPG-GC_2. A very viscous light-yellow oil was recovered (2.17 g, 75%). The final polymer was fully characterized by 1D and 2D

NMR spectroscopy, showing almost quantitative functionalization (98%) of PBD-OH_2, and by SEC analysis (Figures S21, S22, S23, S24).

All the polymer-GC_2 samples were recovered as colorless to light yellow oils.

Poly(hydroxyurethane)s synthesis. In a typical polymerization, PPG-GC_2 (0.150 g, 0.224 mmol) and JEFFAMINE (M_n = 230 g.mol^{-1}, 0.051 g, 0.224 mmol; 1.0 equiv.) were mixed together as neat reagents (*i.e.*, bulk reaction) at 80 °C over 16 h (Table 2, entry 9). Various additives and molar mass of JEFFAMINE have been instigated. Monitoring of the reaction by FTIR then showed the complete disappearance of the 1,3-dioxolan-2-one (GC) band concomitant with the appearance of the urethane band at ν 1740 cm^{-1}. The PHUs/NIPUs were then characterized by SEC either in THF at 35 °C (low molar mass PHUs) or in DMF at 80 °C (high molar mass PHUs).

Results and Discussion

The poly(hydroxyurethane)s (PHUs) were prepared following a two-step strategy involving: 1) the chemical modification of preformed α,ω-dihydroxy telechelic polymers into the corresponding α,ω-di(glycerol carbonate) telechelic pre-polymers, and 2) their subsequent reaction with JEFFAMINEs (Schemes 1-3).

In the first step, the aliphatic α,ω-diols pre-polymers, namely PPG-OH_2, PEG-OH_2, PEE-OH_2, and PBD-OH_2, were each reacted with GC-OTs (Schemes 2,3). The terminal hydroxyl groups were first deprotonated upon reaction with sodium hydride in THF at 23 °C and next coupled with GC-OTS resulting in the formation of the polymers-GC_2 upon elimination of sodium tosylate (Scheme 2). The latter reagent is known to provide convenient linking with alcohols, thiols, amines and other nucleophiles.[13-15] In fact, almost quantitative conversion (96-99 % yields) of both hydroxyl chain-end groups was achieved with each of the polymer diols.

Using PPG-OH_2 pre-polymers of different molar mass (Table 1) as models, we observed, unsurprisingly, that the higher the molar mass of the PPG-OH_2, the less accessible the terminal hydroxyl groups for tosylation, and thus the lower their reactivity (Figure S3). The GC-OTs functionalization procedure did not affect the polymers integrity as evidenced by unchanged molar mass values in SEC (Table 1, and Table S1, S2, S3).

Formation of the various GC-functionalized polymers was then demonstrated from NMR (^{1}H, ^{13}C, COSY, DEPT) and FTIR spectroscopic and MALDI-ToF mass spectrometric analyses. As illustrated Figure 1 in the case of PPG_{400}-OH_2 (Table 1), the characteristic ^{1}H NMR signal of the methylene hydrogens (δ 3.65 ppm; Figure S4) adjacent to the terminal hydroxyl group completely disappeared, concomitantly to the appearance of the new signals diagnostic of the methylene (δ 2.64, 2.82 and 4.27, 4.07 ppm) and methine (δ 3.22 ppm) hydrogens of the GC end-moieties. Correspondingly, the ^{13}C{^{1}H} NMR spectrum of PPG_{400}-GC_2 similarly displayed the characteristic carbonyl peak of GC (δ 154.3. ppm), along with the awaited –CH and (δ 68.3 ppm) and –CH_2 (δ 48.0, 44.2 ppm) signals (Figure 2). Both the ^{1}H-^{1}H COSY and ^{1}H-^{13}C (DEPT) ^{1}H-^{13}C HMQC NMR spectra of α,ω-dicyclocarbonate end-functionalized PPGs corroborated the chemical structure of the polymers and of their termini (Figures S5-S6). The disappearance of the terminal hydroxyl group of PPG_{400}-OH_2 precursor (ν_{OH} 3500 cm^{-1}) was clearly evidenced by FTIR which also further confirmed the presence of the GC end-carbonyl group with its typical strong $\nu_{C=O}$ observed at 1724 cm^{-1} (Figure 3).

Table 1. α,ω-Dihydroxy (PPG-OH_2) and di(glycerol carbonate) (PPG-GC_2) telechelic PPGs characteristics.

	$M_{n,NMR}$ [a] (g.mol^{-1})	$M_{n,SEC}$ [b] (g.mol^{-1})	$Đ_M$ [b]
PPG_{400}-OH_2	430	450	1.13
PPG_{400}-GC_2	670	500	1.26
PPG_{1600}-OH_2	1600	1450	1.10

PPG_{1600}-GC_2	1850	1800	1.21
PPG_{2800}-OH_2	2800	3200	1.04
PPG_{2800}-GC_2	3100	3550	1.19

[a] Determined by NMR analysis of the isolated polymer, from ^{1}H resonances of both terminal groups (refer to the Experimental Section). [b] Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).

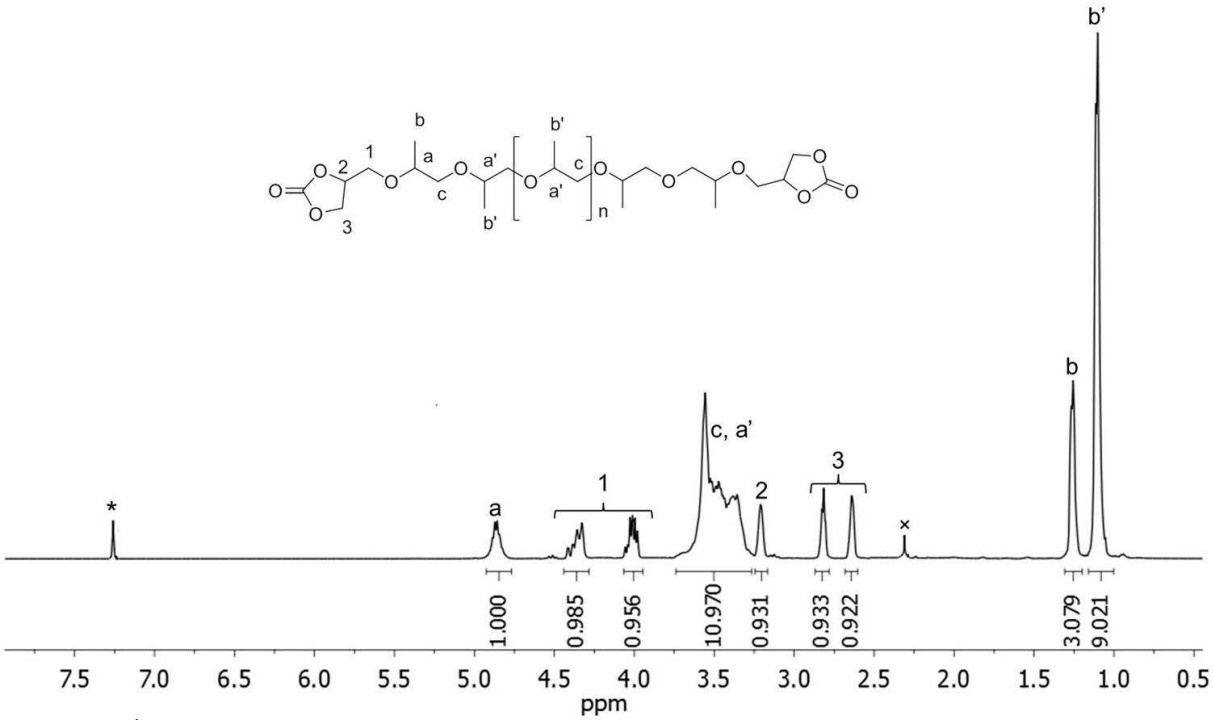


Figure 1. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PPG_{400}-GC_2 (* stands for residual solvent resonances, [x] stands for some unidentified impurity).

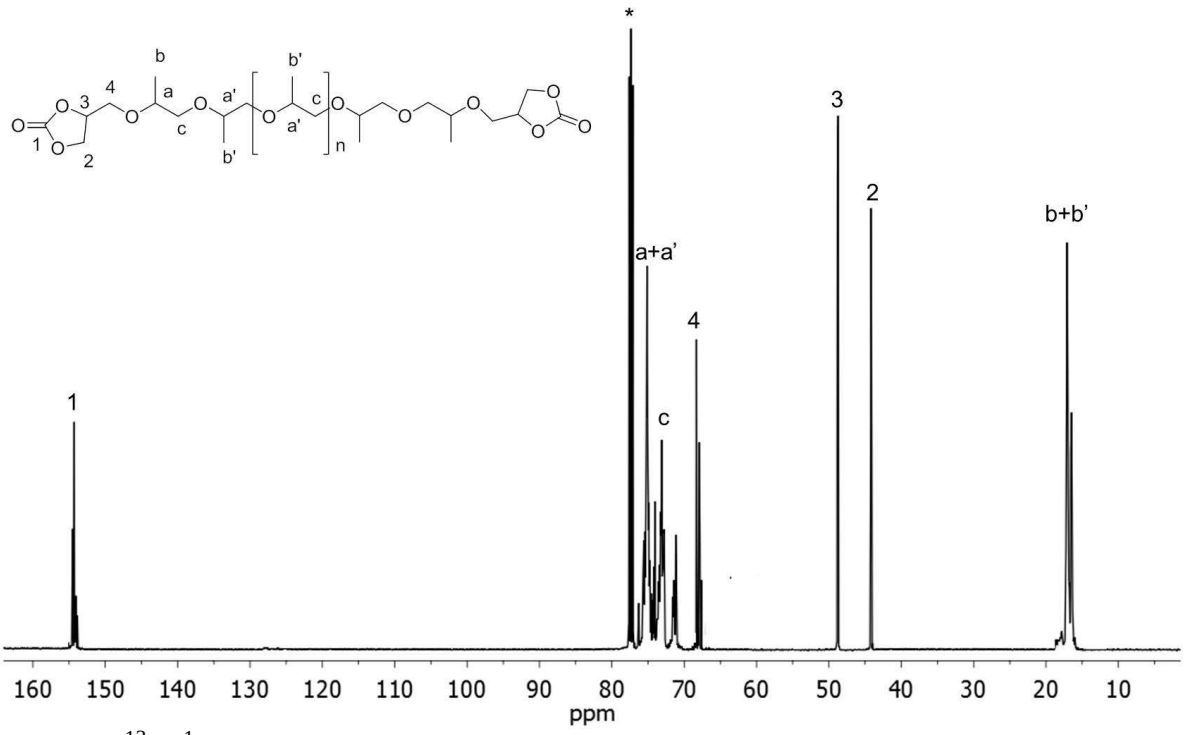


Figure 2. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of PPG_{400}-GC_2 (* stands for residual solvent resonances).

In a same approach, α,ω-dihydroxy telechelic PEGs with different molar mass (PEG_{400}, PEG_{4000}) were chemically modified (*ca.* 80% yield) at both hydroxyl termini into the corresponding PEG-GC_2, without alteration of the polyester backbone (Scheme 2; Table S1). Characterizations of the PEG-GC_2 samples by NMR (^{1}H, ^{13}C, ^{1}H-^{1}H COSY) and FTIR, in comparison to the corresponding PEG-OH_2 analyses (PEG_{400}-OH_2; Figure S7), clearly showed the selective functionalization of the hydroxyl chain-end groups by the desired GC moiety (Figures S8, S9, S10, S11). Also, α,ω-dihydroxy telechelic poly(ester ether), PEE-OH_2 (M_n =1000 g.mol^{-1}; Figures S12, S13) was used in a same procedure to prepare the corresponding α,ω-di(glycerol carbonate) telechelic poly(ester ether), PEE-GC_2 (M_n = 1200 g.mol^{-1}; Table S2). Spectroscopic analyses of this PEE-GC_2 by NMR (Figures S14, S15, S16, S17), FTIR (Figure S18) and MALDI-ToF MS (Figure S19) similarly supported the quantitative functionalization (>98% yield) of the diol precursor into the expected PEE-GC_2.

Motivated by the generalization of the procedure to other non-polyester type polymers and by the possibility to access materials with reactive internal C=C bonds, the approach was next extended to a polydiene. Modification of an α,ω-dihydroxy telechelic poly(butadiene), PBD-OH_2 (Figure S20), into the corresponding GC-end capped polymer, PBD-GC_2, using the GC-Ts route, revealed also efficient). The polymer backbone remained unaffected by the reaction, and the successful functionalization by GC (98% yield) was attested by NMR (^{1}H, ^{13}C, COSY) and FTIR analyses (Figures S21, S22, S23, and S24 and Table S3, respectively).

In a second step, the primary polyether-diamines differing in molar mass, JEFFAMINEs (JA), were reacted with the α,ω-di(glycerol carbonate) PPG_{400} pre-polymer, using a constant equimolar polymer/amine ratio, thereby affording the corresponding PHUs/NIPUs, PPG_{400}HU. Several PHUs were thus prepared from PPG_{400}-GC_2 ($M_{n,NMR}$ = 670 g.mol^{-1}; Table 1) used as model, while varying the molar mass of the amine (JA_{230}, JA_{400}, JA_{2000} with M_n = 230, 400, and 2000 g.mol^{-1}, respectively), the nature of the additive (LiBr, $ZnCl_2$, ^{t}BuOK, LiOTf, $Sc(OTf)_3$, $Al(OTf)_3$, $In(OTf)_3$, dibutyl tin laurate (DBTL) with OTf = CF_3SO_3), the reaction time (16 h or 48 h), or the reaction temperature (25, 50 or 80 °C) (Scheme 3).

In the absence of any additive, the reaction temperature demonstrated a more significant impact on the efficiency of the polyaddition of PPG_{400}-GC_2 with JA_{230}, than a prolonged reaction time. Indeed, the conversion of PPG_{400}-GC_2 monitored over 16 h progressively increased from 25 to 67% upon going from 25 to 80 °C, respectively (Table 2, entries 1-3), whereas for a given reaction temperature (25, 50 or 80 °C), the conversion of the PPG_{400}-GC_2 into the corresponding PPG_{400}HU was hardly improved with a longer reaction time period (16 to 48 h; Table 2 entries 2 vs 4 and 3 vs 5). With JA_{230}, under these experimental conditions, the PPG_{400}HU molar mass did not exceed $M_{n,SEC}$ = 20,000 g.mol^{-1}. FTIR monitoring of the polymerization from PPG_{400}-OH_2 via PPG_{400}-GC_2 (*vide supra*) to

$PPGHU_{400}$ ultimately showed, the broadening of this C=O stretch absorption to also encompass a urethane-amide I band $\nu_{C=O}$ at 1740–1720 cm^{-1}, while the corresponding amide II band was observed at ν_{C-N} 1550 cm^{-1}, along with the increase of the ν_{NH} band at 3330 cm^{-1} somewhat overlapping with the ν_{OH} at 3500 cm^{-1}, as hinted by the spectrum of the PPG_{400}-OH_2 precursor (possibly suggesting the occurrence of hydrogen bonding in the PHU samples) (Figure 3). Use of higher molar mass JEFFAMINEs (JA_{400} and JA_{2000}; M_n = 400 and 2000 $g.mol^{-1}$, respectively), still in absence of any added additive, at 50/80 °C and over 48 h, enabled the formation of PHUs of significantly higher molar mass ($M_{n,SEC}$ up to 68,000 $g.mol^{-1}$) as determined by SEC in DMF (Table 2, entries 6-9). The dispersity of all the PPG_{400}HUs prepared remained below $Đ_M$ = 2.6 (Table 2).

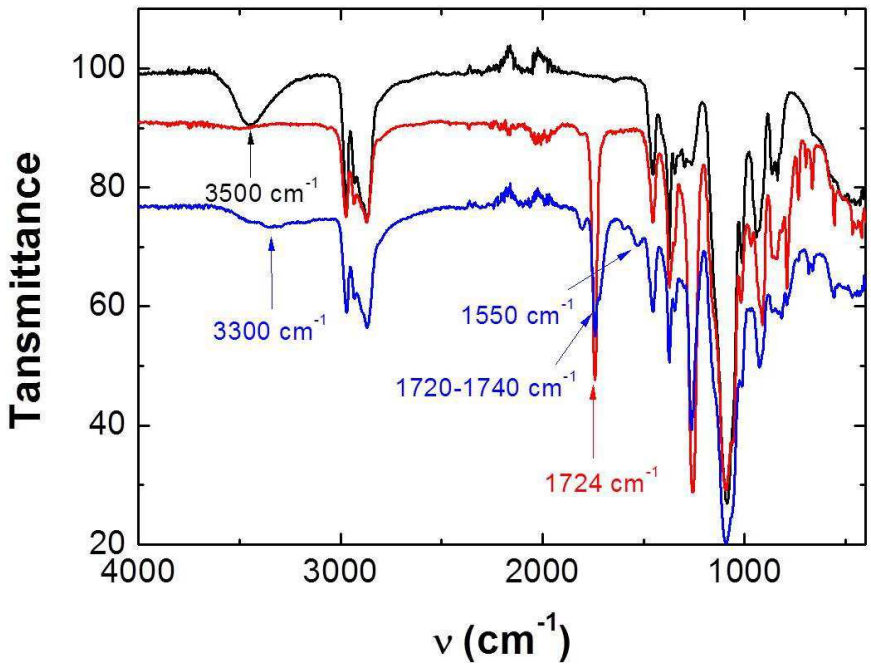


Figure 3. FTIR spectra of PPG_{400}-OH_2 (top black trace) and of the resulting PPG_{400}-GC_2 (middle red trace) and PPG_{400}HU after reaction with JA_{230} (bottom blue trace) (Table 2, entry 5).

Table 2. Reaction of PPG_{400}-GC_2 with JEFFAMINEs at different reaction temperatures without an additive.[a]

Entry	Temp. (°C)	Reaction time (h)	JEFFAMINE	Conv.[b] (%)	$M_{n,SEC}$[c] ($g.mol^{-1}$)	$Đ_M$[c]
1	25	16	JA_{230}	25	1100	1.8
2	50	16	JA_{230}	50	1900	2.3
3	80	16	JA_{230}	67	6050	2.3
4	25	48	JA_{230}	31	5900	2.0
5	50	48	JA_{230}	59	10,700	2.4
6	80	48	JA_{230}	78	20,000	2.2
7	50	48	JA_{400}	89	25,000	2.5
8	80	48	JA_{400}	-[d]	49,000	2.4
9	50	48	JA_{2000}	-[d]	45,000	2.6
10	80	48	JA_{2000}	-[d]	68,000	2.3

[a] Polymerization conditions: PPG_{400}-GC_2 = 0.150 g; [PPG_{400}-GC_2]/[JA] = 1.0. [b] Determined by NMR analysis of the isolated polymer. [c] Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected M_n values). [d] The low intensity of the chain-end signals precluded accurate determination of the conversion.

In order to promote the cyclocarbonate/amine reaction, different additives were evaluated in the present study, namely LiBr, $ZnCl_2$, ^{t}BuOK, LiOTf, $M(OTf)_3$ (M = Sc, Al, In), or DBTL, to assess their influence on the PPG-GC_2/diamine reaction. The role of these additives in promoting the formation of PHU/NIPU from PPG_{400}-GC_2 has been evaluated by performing three sets of experiments at different temperatures: 25 °C, 50 °C and 80 °C (Tables 3, 4, 5, respectively). No matter the reaction temperature, LiBr revealed the most efficient (yet still modestly) additive, affording the highest PPG_{400}-GC_2 conversion, as evaluated by NMR monitoring of the signals of the GC chain-end groups. Using 5 mol% of LiBr, the conversion was slightly improved to 45–80% as compared to the LiBr-free (25–67%) PPG_{400}-GC_2/JA_{230} polyaddition (Tables 3–5, entries 1 *vs*. 2). Along with such an enhanced reactivity, the procedure ran at 80 °C afforded a higher molar mass PHU/NIPU (M_n = 15,700 $g.mol^{-1}$, Table 5, entry 2) as compared to the oligomers formed without LiBr at 20 °C (M_n = 1100 $g.mol^{-1}$; Table 3, entry 1). At the opposite, $In(OTf)_3$ seemed ineffective, affording a conversion varying from 22 to 65% upon raising the temperature from 25 to 80 °C

(Tables 3–5, entry 8), similar to that obtained in absence of an additive (Tables 3–5, entry 1). All other additives evaluated all ranked in between these two extremes, with LiOTf, DBTL and ^{t}BuOK standing higher than the other metal triflates (M = Sc, Al, In) or $ZnCl_2$. The tentative rationalization of such an order of reactivity among these additives is that LiBr supposedly provides (to some extent, *vide infra*) better fluidity to the reaction medium than the others, upon cleaving more effectively the hydrogen bonds formed concomitantly to the synthesis of the PHUs/NIPUs. Finally, the synthesis of PPGHUs from PPG_{400}-GC_2 was carried out in presence of a few of these additives (5 mol%), at 80 °C in presence of the various JEFFAMINEs over 16h (Table 6). The experiments were preferentially run over a shorter reaction time (16h *vs*. 48h) so as to avoid the increase in viscosity of the reaction medium. Indeed, longer reaction times would most likely afford higher molar mass PHUs as observed in Table 2, but the objective of the present work was rather to demonstrate the feasibility of the approach rather than focusing on longer PHUs. Increasing the molar mass of the diamine resulted in a significant increase of the viscosity of the reaction medium and in higher molar mass PHUs. As a consequence, the low intensity of the chain-end signals in the NMR spectra precluded accurate determination of the conversion. The molar mass of the JEFFAMINE did not affect significantly the molar mass and the dispersity values of the PHUs recovered remained within the same range, regardless of the additive used. Under such operating conditions, high molar mass PPGHUs ($M_{n,SEC} \leq$ 52,300 g.mol^{-1}) were prepared with $Đ_M \leq 2.6$.

Table 3. Reactions of PPG_{400}-GC_2 with JEFFAMINE JA_{230} at 25 °C over 16 h, in presence of various additives.

Entry	Additive [a] (5 mol%)	Conv. [b] (%)	$M_{n,SEC}$ [c] (g.mol^{-1})	$Đ_M$ [c]
1	-	25	1100	1.8
2	LiBr	45	4300	2.3

3	$ZnCl_2$	30	2800	2.3
4	^{t}BuOK	40	3200	2.4
5	LiOTf,	35	2800	2.2
6	$Sc(OTf)_3$	30	3500	2.5
7	$Al(OTf)_3$	28	2900	2.4
8	$In(OTf)_3$	22	1200	2.6
9	DBTL	38	3800	2.3

[a] Polymerization conditions: PPG_{400}-GC_2 = 0.150 g; PPG_{400}-GC_2 : JA = 1. [b] Determined by NMR analysis. [c] Determined by SEC in THF at 30 °C or DMF at 60 °C *vs*. polystyrene standards (uncorrected M_n values).

Table 4. Reaction of PPG_{400}-GC_2 with JEFFAMINE JA_{230} at 50 °C over 16 h, in presence of various additives.

Entry	Additive [a] (5 mol%)	Conv. [b] (%)	$M_{n,SEC}$ [c] ($g.mol^{-1}$)	$Đ_M$ [c]
1	-	50	1900	2.3
2	LiBr	66	6300	2.2
3	$ZnCl_2$	53	4800	2.3
4	tBuOK	57	5200	2.3
5	LiOTf,	60	5600	2.2
6	$Sc(OTf)_3$	52	2900	2.6
7	$Al(OTf)_3$	55	3700	2.2
8	$In(OTf)_3$	52	2900	2.5
9	DBTL	60	5800	2.4

[a] Polymerization conditions: PPG_{400}-GC_2 = 0.150 g; PPG_{400}-GC_2 : JA = 1. [b] Determined by NMR analysis of the isolated polymer. [c] Determined by SEC in THF at 30 °C or DMF at 60 °C *vs*. polystyrene standards (uncorrected M_n values).

Table 5. Reaction of PPG_{400}-GC_2 with JEFFAMINE JA_{230} at 80 °C over 16 h, in presence of various additives.

Entry	Additive [a] (5 mol%)	Conv. [b] (%)	$M_{n,SEC}$ [c] ($g.mol^{-1}$)	$Đ_M$ [c]
1	-	67	6030	2.3
2	LiBr	80	15,700	2.2
3	$ZnCl_2$	69	12,300	2.3
4	tBuOK	71	13,100	2.3
5	LiOTf,	73	15,300	2.2
6	$Sc(OTf)_3$	70	13,200	2.6
7	$Al(OTf)_3$	75	12,800	2.2

8	$In(OTf)_3$	65	5600	2.5
9	DBTL	73	14,600	2.4

[a] Polymerization conditions: PPG_{400}-GC_2 = 0.150 g; PPG_{400}-GC_2 : JA = 1. [b] Determined by NMR. [c] Determined by SEC in THF at 30 °C or DMF at 60 °C *vs*. polystyrene standards (uncorrected M_n values).

Table 6. Reactions of PPG_{400}-GC_2 with various JEFFAMINE JA_{400} and JA_{2000} at 80 °C over 16 h, in the presence of various additives.

Entry	JEFFAMINE	Additive [a] (5 mol%)	Conv. [b] (%)	$M_{n,SEC}$ [c] ($g.mol^{-1}$)	$Đ_M$ [c]
1	JA_{400}	-	57	15,000	2.2
2	JA_{400}	LiBr	- [d]	35,700	2.5
3	JA_{400}	$ZnCl_2$	- [d]	30,300	2.3
4	JA_{400}	LiOTf,	- [d]	37,800	2.2
5	JA_{400}	$Sc(OTf)_3$	- [d]	30,400	2.4
6	JA_{400}	$Al(OTf)_3$	- [d]	28,800	2.3
7	JA_{2000}	-	- [d]	22,200	1.9
8	JA_{2000}	LiBr	- [d]	45,100	2.3
9	JA_{2000}	$ZnCl_2$	- [d]	32,400	2.5
10	JA_{2000}	LiOTf,	- [d]	40,800	2.6
11	JA_{2000}	$Sc(OTf)_3$	- [d]	28,700	2.5
12	JA_{2000}	$Al(OTf)_3$	- [d]	52,300	2.4

[a] Polymerization conditions: PPG_{400}-GC_2 = 0.150 g; PPG_{400}-GC_2 : JA = 1. [b] Determined by NMR analysis. [c] Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected *M*n values). [d] The low intensity of the chain-end signals in the NMR spectra precluded accurate determination of the conversion.

Conclusion

The chemical modification of various polymer-diols, PPG-, PEG-, PEE-, or PBD-OH_2, into the corresponding polymers α,ω-end functionalized by glycerol carbonate, through reaction with GC-OTs, provides a convenient and effective direct procedure, which can be applied to different families of polymers, namely polyethers, polyesters and polydienes. This original simple strategy towards polymers-GC_2 is a more straightforward pathway than the previously established two-step approach involving the successive modification of the

hydroxyl termini into carboxylic groups subsequently coupled to glycerol carbonate.[5] Also, it offers a valuable complementary pathway toward the preparation of similarly GC-telechelic polydienes, which can be obtained by ruthenium-catalyzed ROMP of cycloolefins in the presence of a glycerol carbonate derivative as chain transfer agent.[6]

Polyhydroxyurethanes were next synthesized in a catalyst-free and isocyanate-free single step, through the neat (*i.e.* solvent-free) carbonate/amine polyaddition of the α,ω-dicyclocarbonate telechelic PPGs (selected for a conceptual demonstration) and JEFFAMINEs (M_n = 230-2000 g.mol^{-1}). A higher reaction temperature or a higher molar mass diamine enabled to prepare higher molar mass PHUs/NIPUs. When the polymerization was carried out in the presence of LiBr introduced as an additive, a slight improvement of the conversion was observed. Well-defined high molar mass PHUs/NIPUs with M_n up to 68,000 g.mol^{-1} were thus smoothly and easily prepared. The selectivity of the polymerization process was confirmed by NMR, FTIR and SEC analyses.

Although the main objective was not to target high molar mass values, the PHUs/NIPUs prepared from polymers-GC_2 pre-polymers rather easily provided, following this one-step carbonate/amine catalyst-free strategy, a large range of molar masses varying from 10,000 < $M_{n,SEC}$ < 68,000 g.mol^{-1}. These molar mass values are, to our knowledge, significantly higher than those reached for PHUs/NIPUs derived from natural vegetable oils through a same five-membered ring cyclic carbonate/diamine isocyanate-free procedure (typically < 20,000 g.mol^{-1})[1,2] and, along with the prior examples reported by Keul,[3b] among the highest ones obtained for PHUs/NIPUs prepared from the amine/carbonate concept (Scheme 1).[16]

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Electronic Supplementary Information (ESI) available: Complementing ^{1}H ,^{13}C , COSY DEPT NMR spectra of GC-OTs, PPG_{400}-OH_2, PEG_{400}-OH_2, PEG_{400}-GC_2, PEE-OH_2, PEE-GC_2, PBD-OH_2, PBD-GC_2, FTIR spectra of PEG_{400}-OH_2, PEG_{400}-GC_2, PEE_{400}-OH_2, PEE_{400}-GC_2, PBD-OH_2. PBD-GC_2, and MALDI-ToF MS of PEE-GC_2 and SEC data for the PEG, PEE, PBD-OH_2 and -GC_2 polymers.

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Electronic Supplementary Information

α,ω-Di(glycerol carbonate) Telechelic Polyesters and Polyolefins as Precursors to PolyHydroxyUrethanes: an Isocyanate-free approach

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances)

Figure S2. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances)

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectra of $PPG_{400,1600,2800}$-GC_2 prepared from the reaction of the corresponding $PPG_{400,1600,2800}$-OH_2 with GC-OTS.

Figure S4. ^{1}H NMR (500 MHz, CDl_3, 25 °C) spectrum of PPG_{400}-OH_2 (* stands for residual solvent resonances, and x stands for an unidentified impurity).

Figure S5. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PPG_{400}-GC_2.

Figure S6. ^{1}H-^{13}C (DEPT) HMQC NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of PPG_{400}-GC_2.

Figure S7. (a) ^{1}H (500 MHz, $CDCl_3$, 25 °C) and (b) $^{13}C\ \{^{1}H\}$ (125 MHz, $CDCl_3$, 25 °C) NMR spectra of PEG_{400}-OH_2.

Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of the PEG_{400}-GC_2.

Figure S9. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of the PEG_{400}-GC_2.

Figure S10. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of the PEG_{400}-GC_2.

Figure S11. FTIR spectra of PEG_{400}-OH_2 (black trace) and the resulting PEG_{400}-GC_2 (red trace).

Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of the PEE-OH_2.

Figure S13. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of the PEE-OH_2.

Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PEE-GC_2 (* marker stands for residual toluene and ** for the starting reagent).

Figure S15. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of PEE-GC_2 (* marker stands for residual toluene).

Figure S16. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of PEE-GC_2.

Figure S17. ^{1}H-^{13}C (DEPT) HMQC NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of PEE-GC_2.

Figure S18. FTIR spectra of PEE-OH_2 (black trace) and the resulting PEE-GC_2 (red trace).

Figure S19. MALDI-ToF MS spectrum of PEE-GC_2.

Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PBD-OH_2.

Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PBD-GC_2 (* marker stands for residual toluene).

Figure S22. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of PBD-GC_2.

Figure S23. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PBD-GC_2.

Figure S24. FTIR spectra of PBD-OH_2 (black trace) and the resulting PBD-GC_2 (red trace).

Scheme S1. Synthesis of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs).

Table S1. α,ω-Dihydroxy and dicyclocarbonate telechelic PEGs characteristics.

Table S2. α,ω-Dihydroxy and dicyclocarbonate telechelic PEE characteristics.

Table S3. α,ω-Dihydroxy and dicyclocarbonate telechelic PBD characteristics.

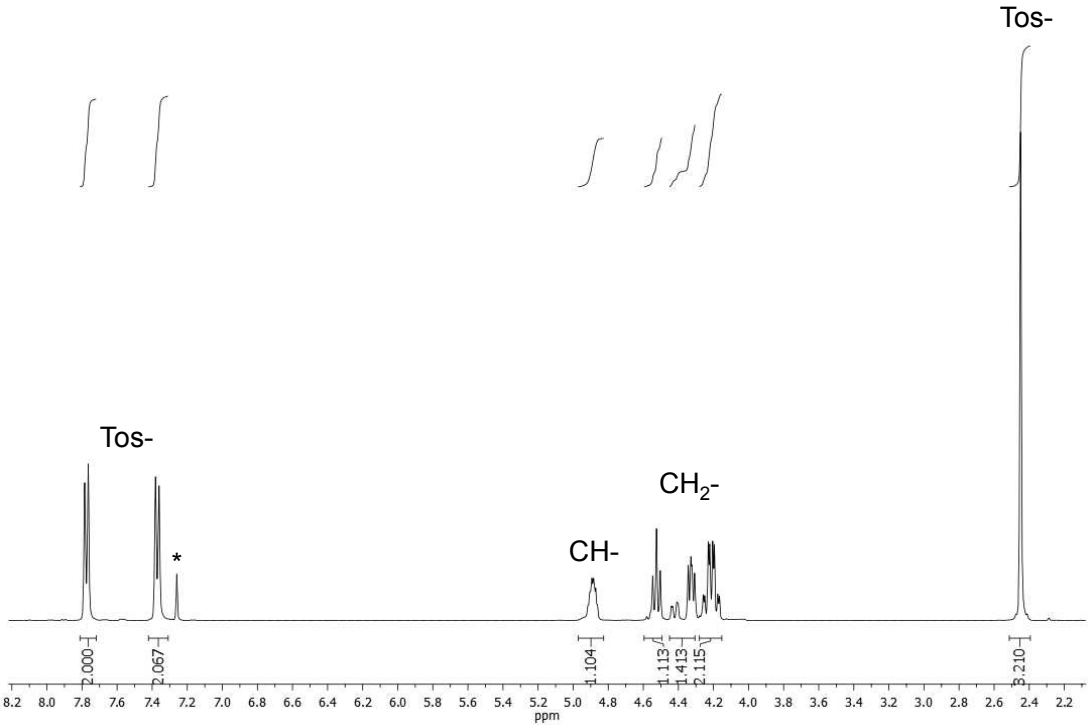

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances).

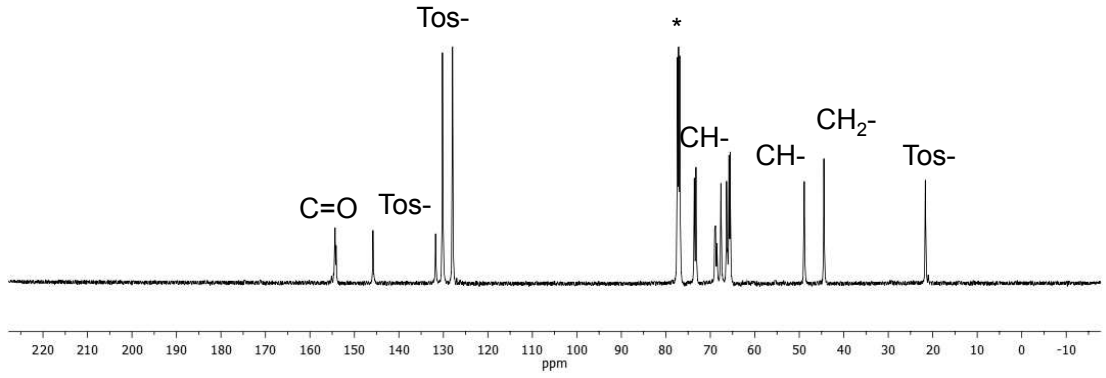

Figure S2. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances).

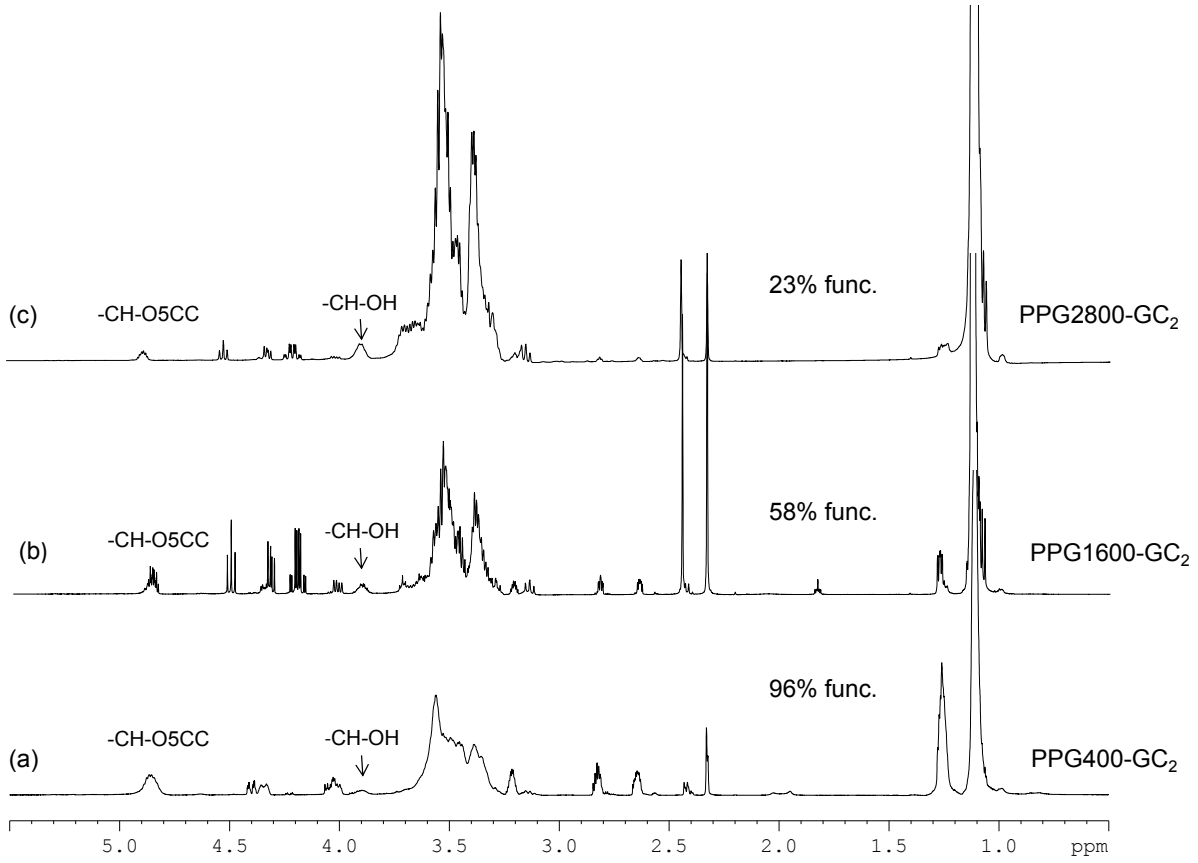

Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectra of $PPG_{400,1600,2800}$-GC_2 prepared from the reaction of the corresponding $PPG_{400,1600,2800}$-OH_2 with GC-OTS.

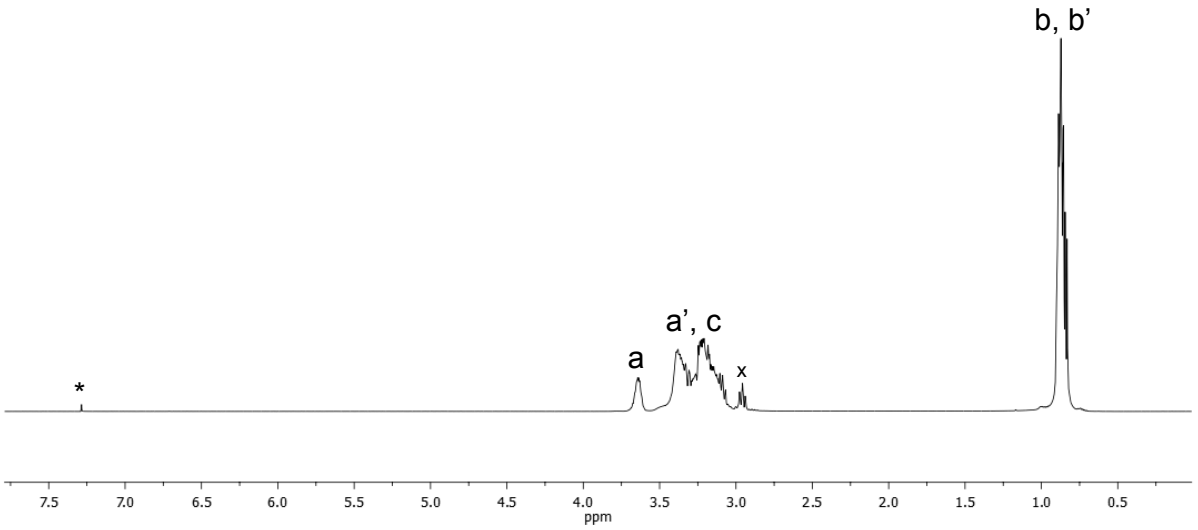

Figure S4. ^{1}H NMR (500 MHz, CDl_3, 25 °C) spectrum of PPG_{400}-OH_2 (* stands for residual solvent resonances, and x stands for an unidentified impurity).

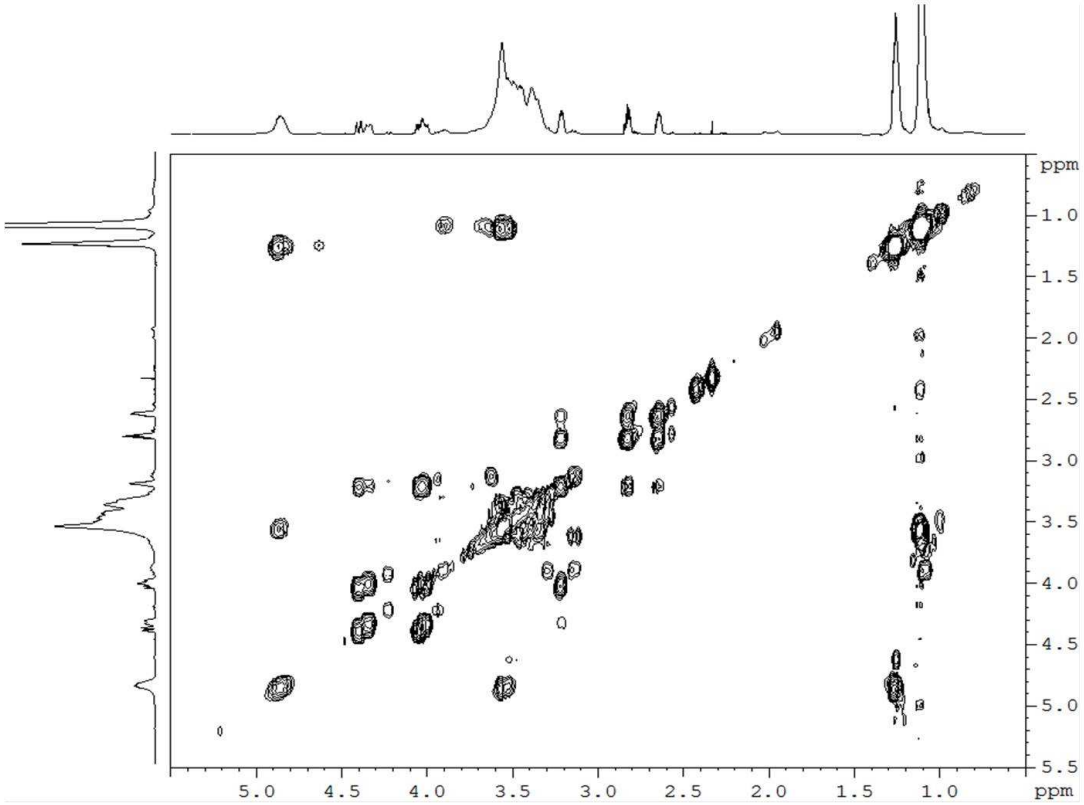

Figure S5. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PPG_{400}-GC_2.

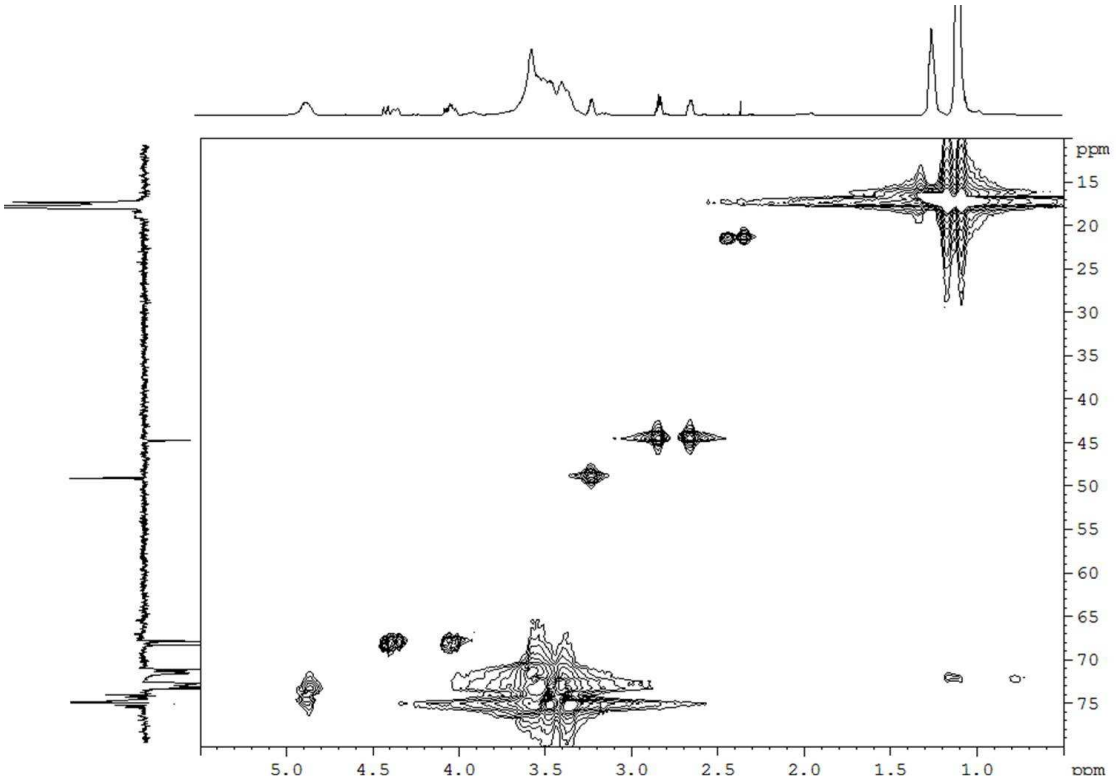

Figure S6. ^{1}H-^{13}C (DEPT) HMQC NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of PPG_{400}-GC_2.

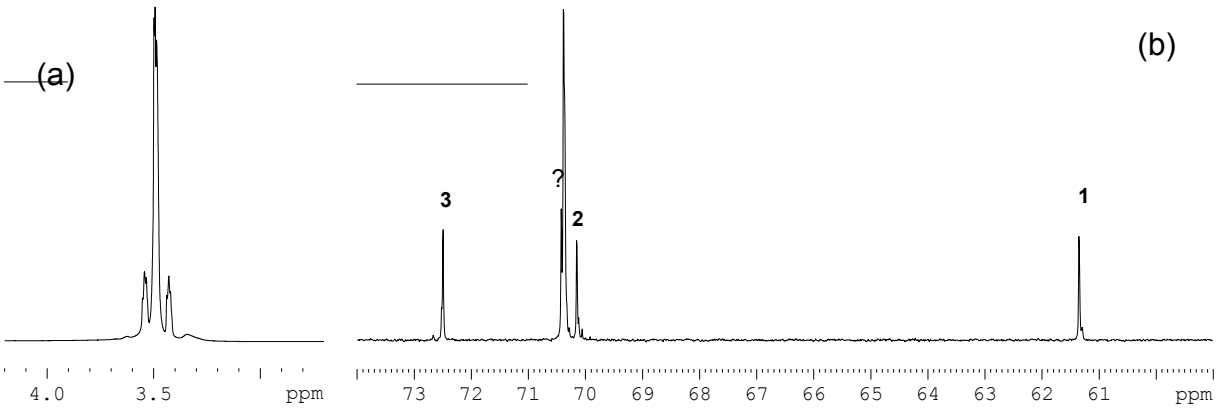

Figure S7. (a) ^{1}H (500 MHz, $CDCl_3$, 25 °C) and (b) ^{13}C {^{1}H} (125 MHz, $CDCl_3$, 25 °C) NMR spectra of PEG_{400}-OH_2.

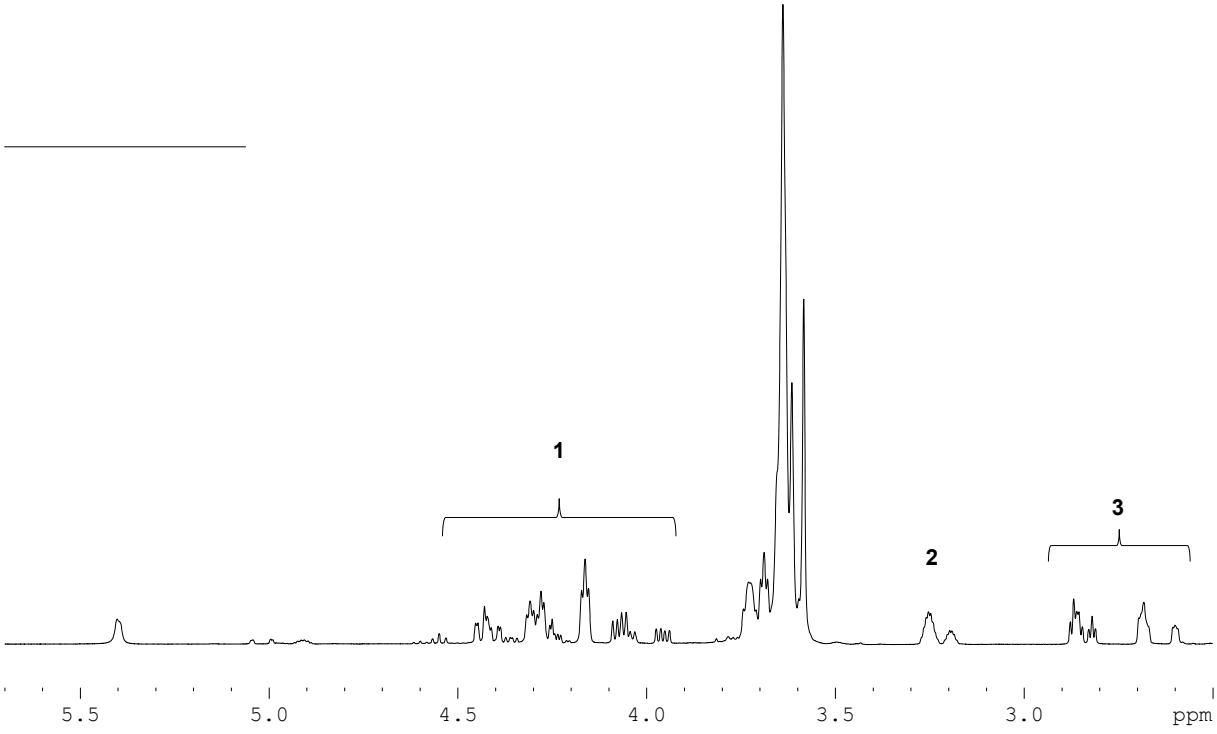

Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of the PEG_{400}-GC_2.

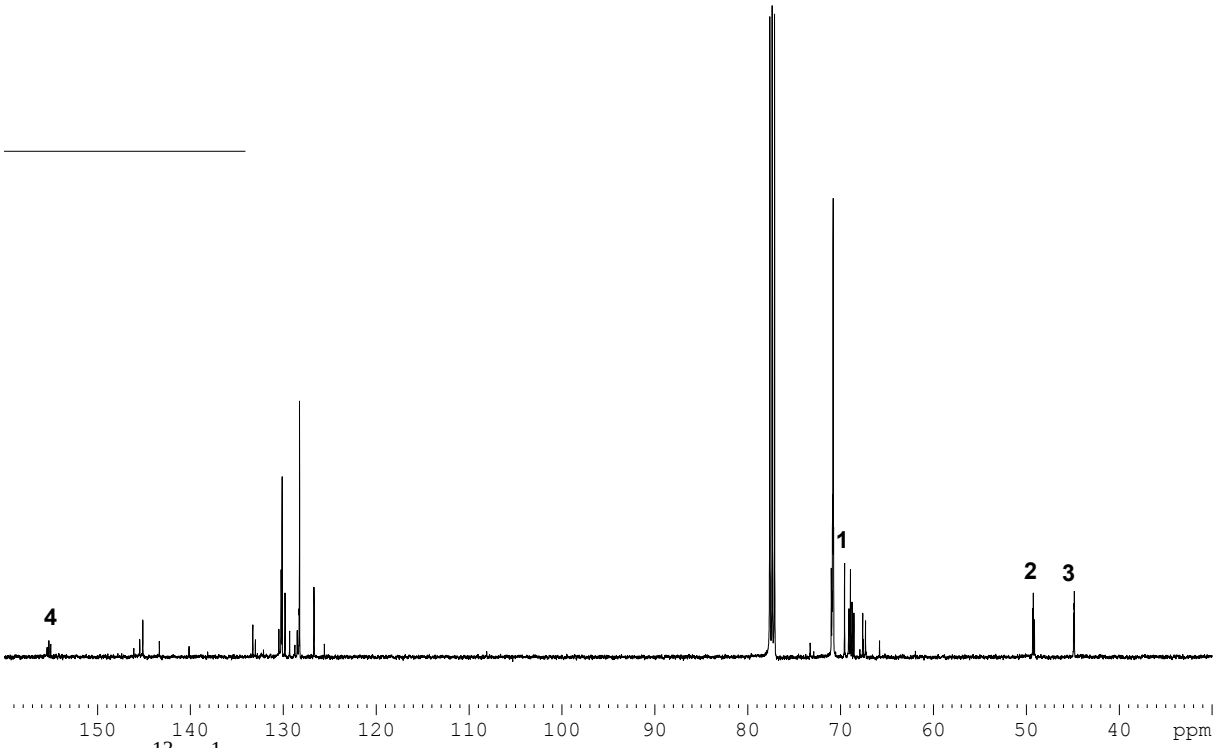

Figure S9. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of the PEG_{400}-GC_2.

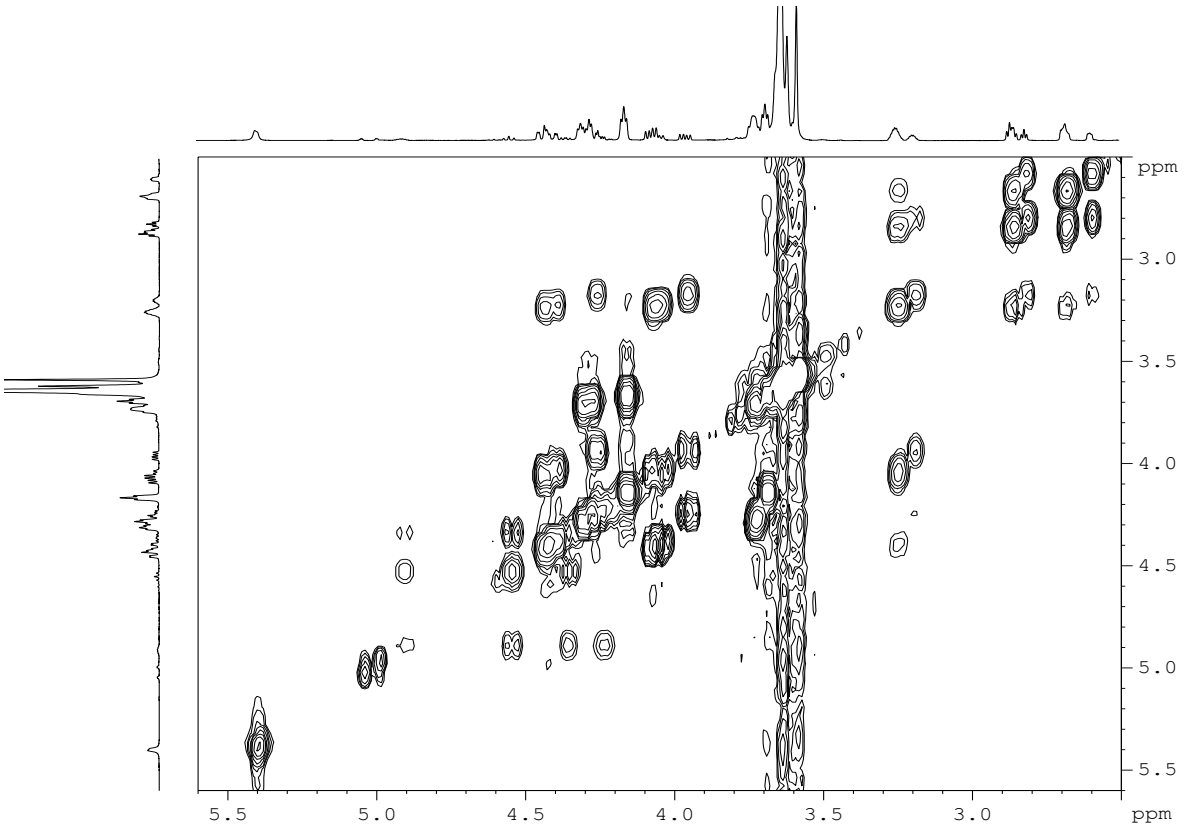

Figure S10. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of the PEG_{400}-GC_2.

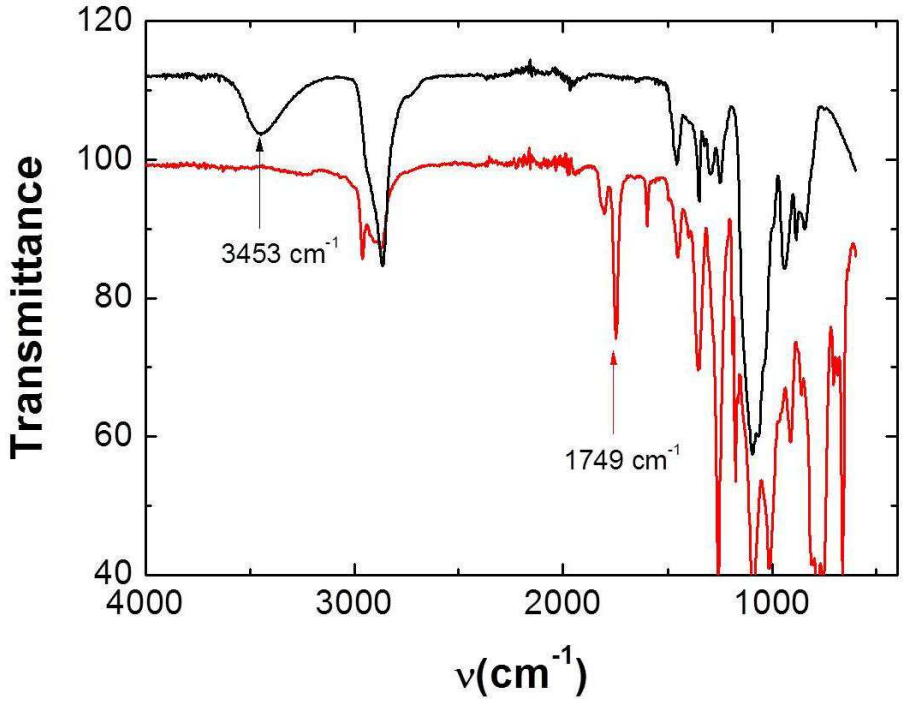

Figure S11. FTIR spectra of PEG_{400}-OH_2 (black trace) and the resulting PEG_{400}-GC_2 (red trace).

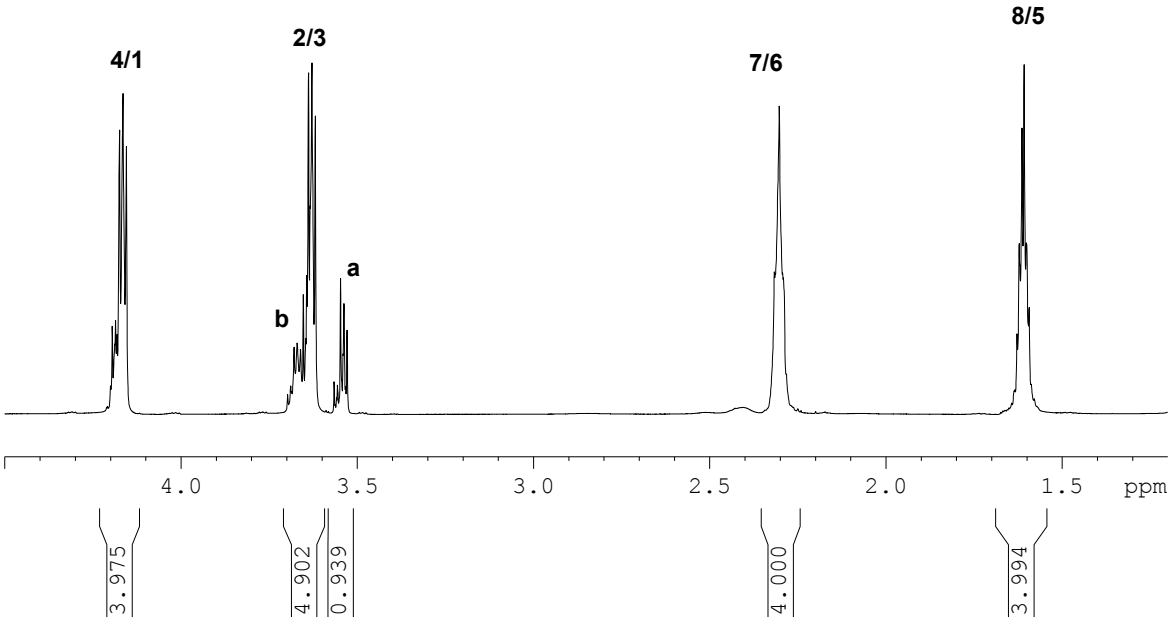

Figure S12. ^1H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of the PEE-OH_2.

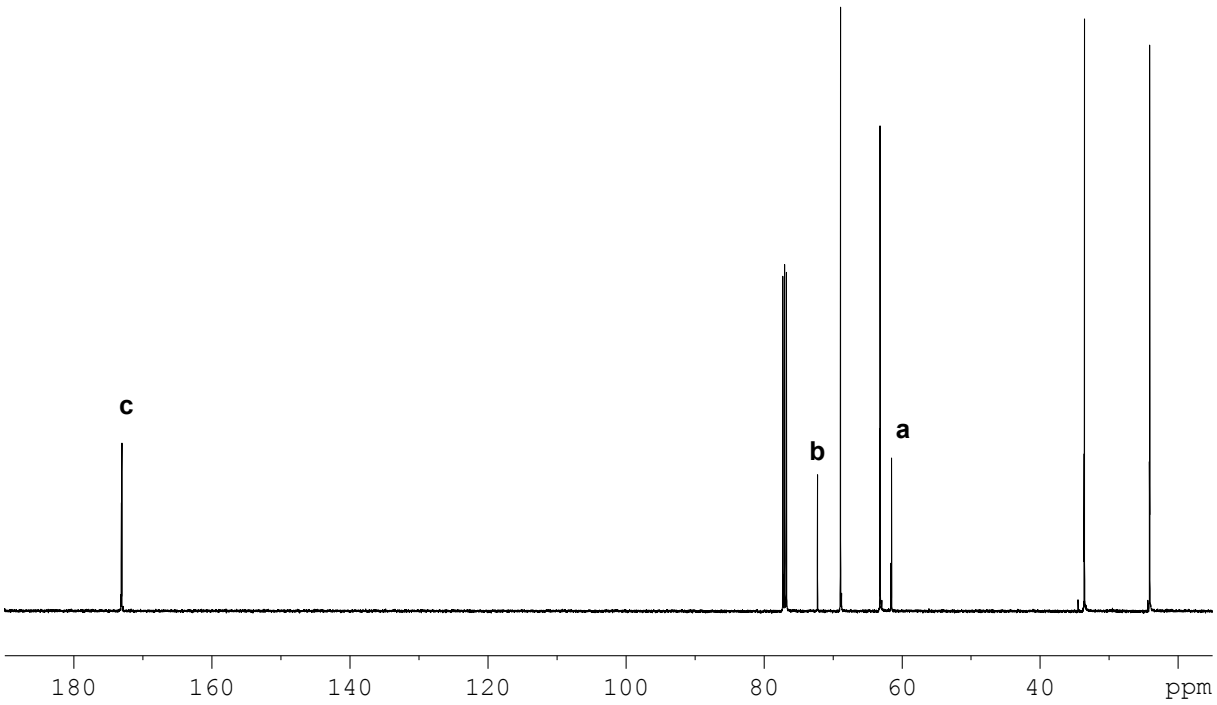

Figure S13. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of the PEE-OH_2.

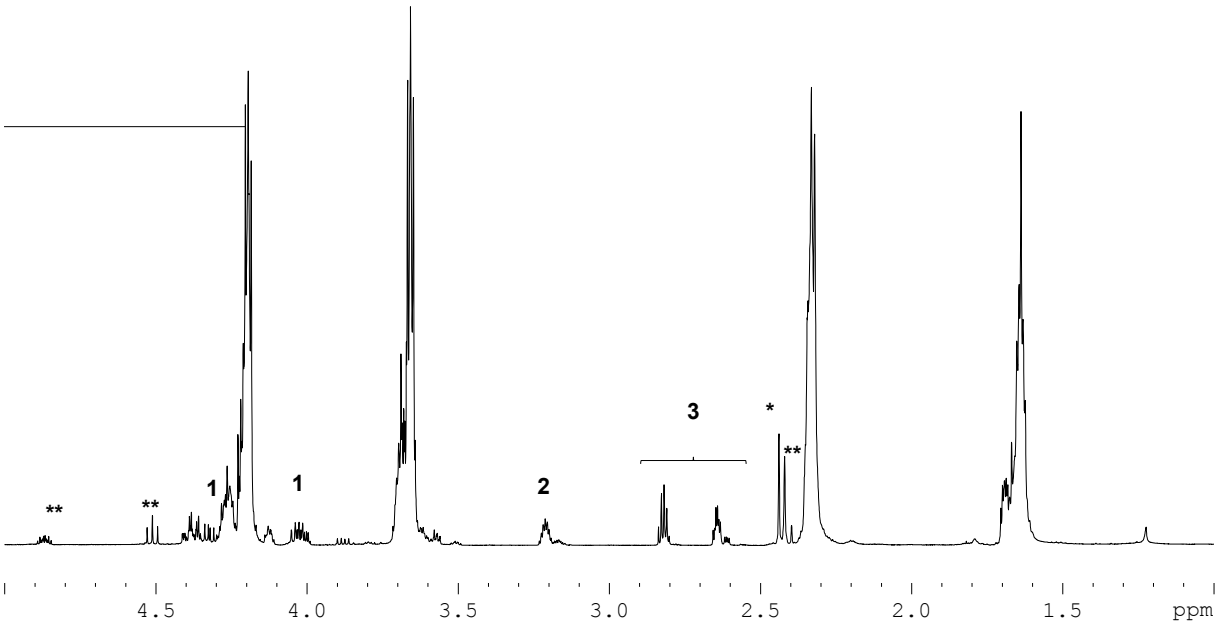

Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PEE-GC_2 (* marker stands for residual toluene and ** for the starting reagent).

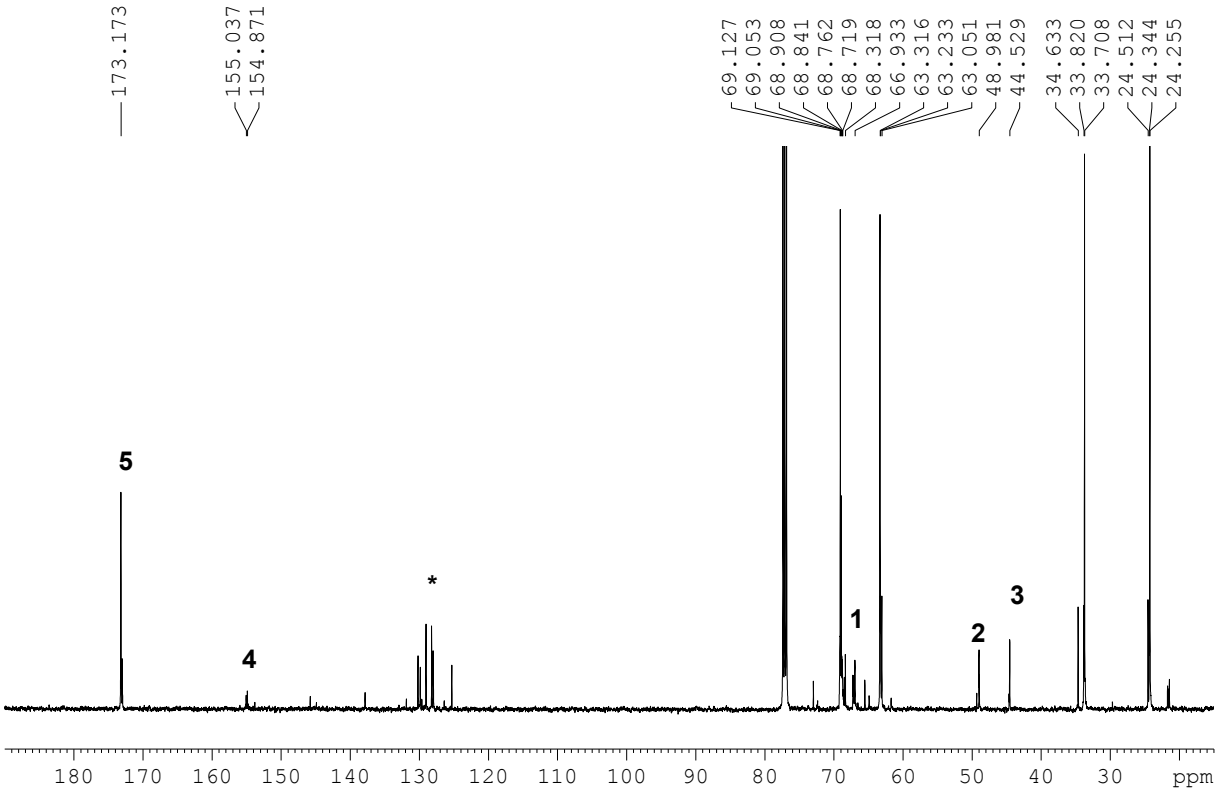

Figure S15. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of PEE-GC_2 (* marker stands for residual toluene).

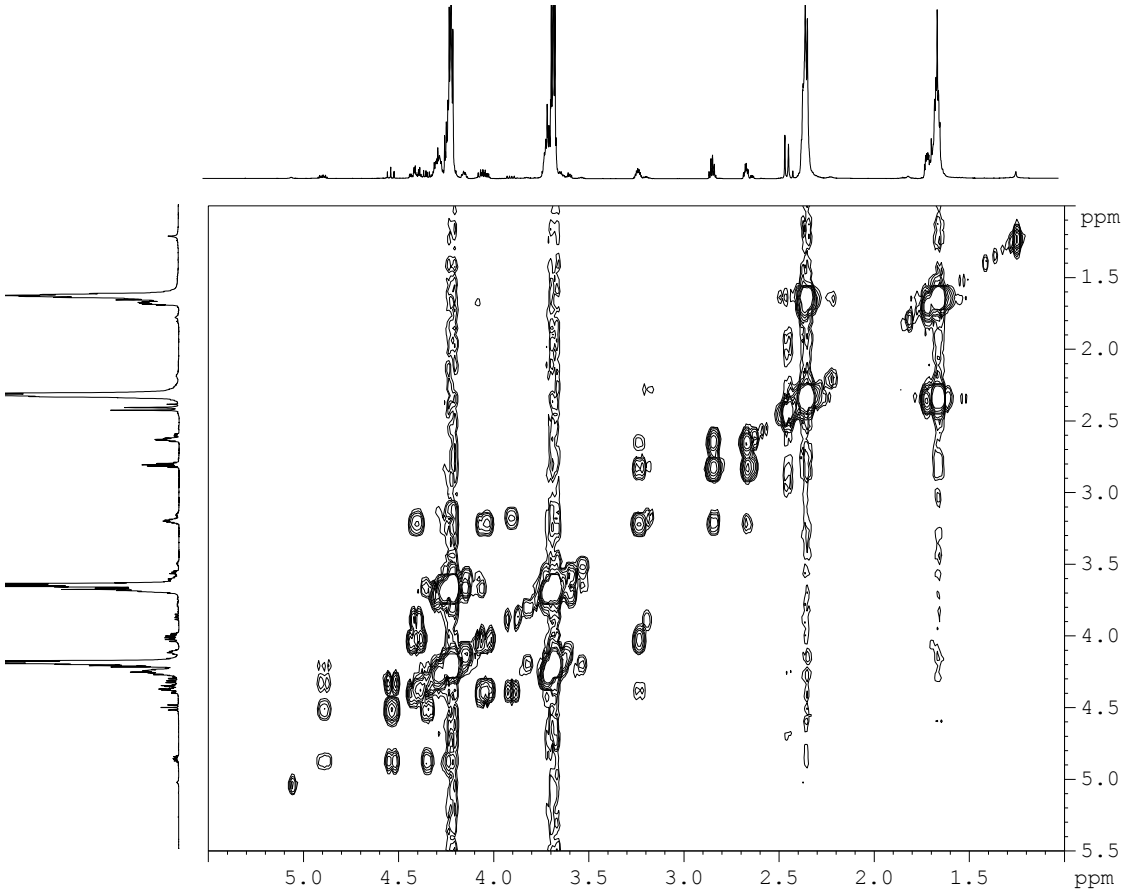

Figure S16. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of PEE-GC_2.

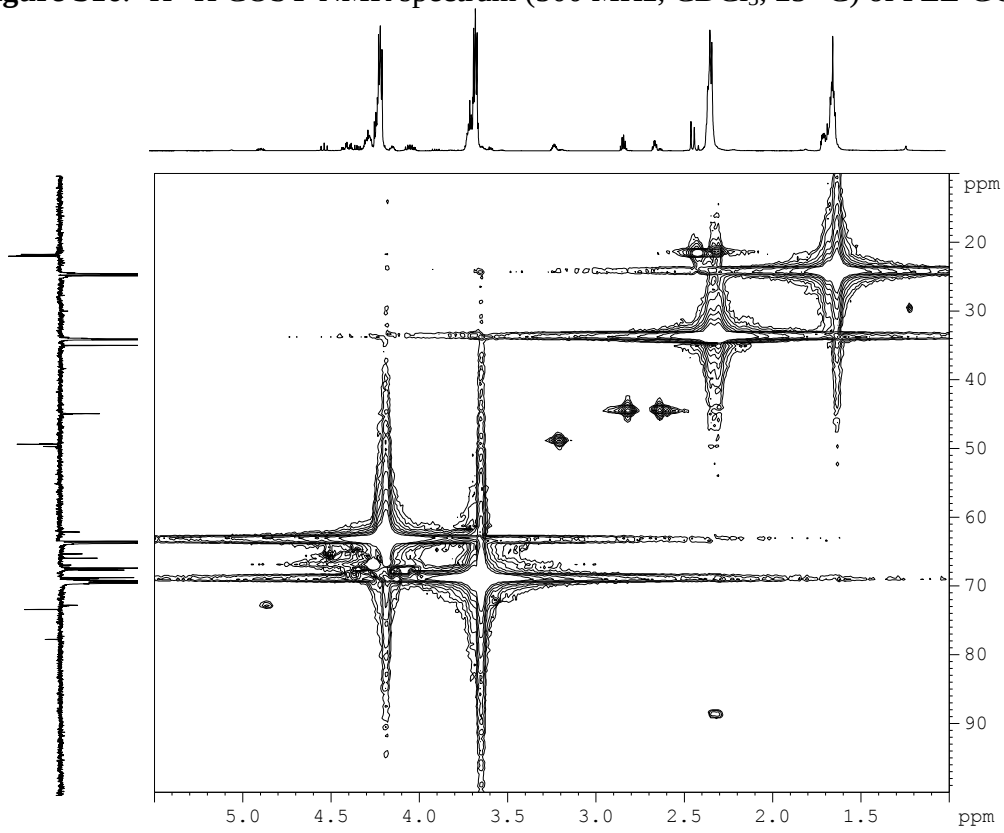

Figure S17. ^{1}H-^{13}C (DEPT) HMQC NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of PEE-GC_2.

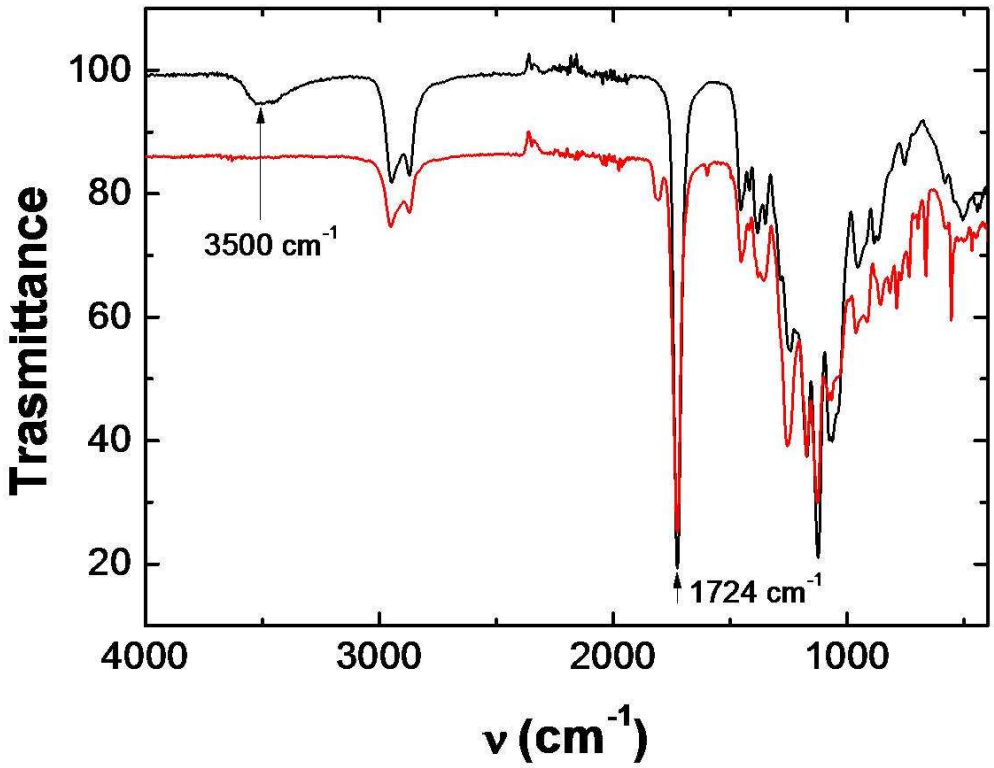

Figure S18. FTIR spectra of PEE-OH_2 (black trace) and the resulting PEE-GC_2 (red trace).

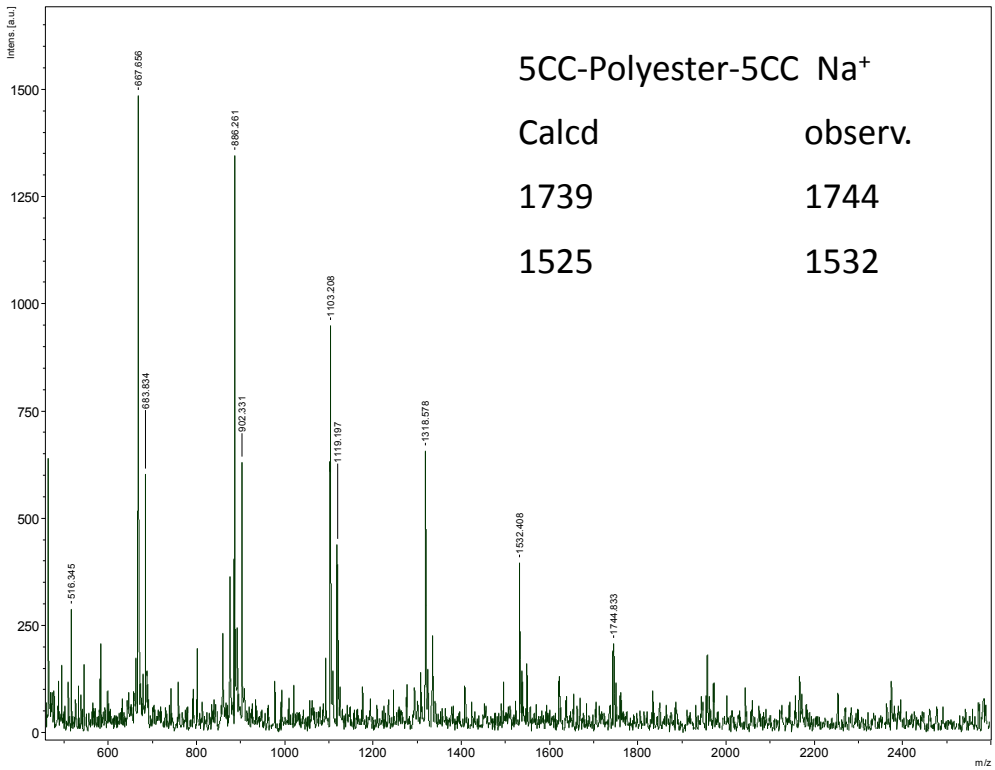

Figure S19. MALDI-ToF MS spectrum of PEE-GC_2.

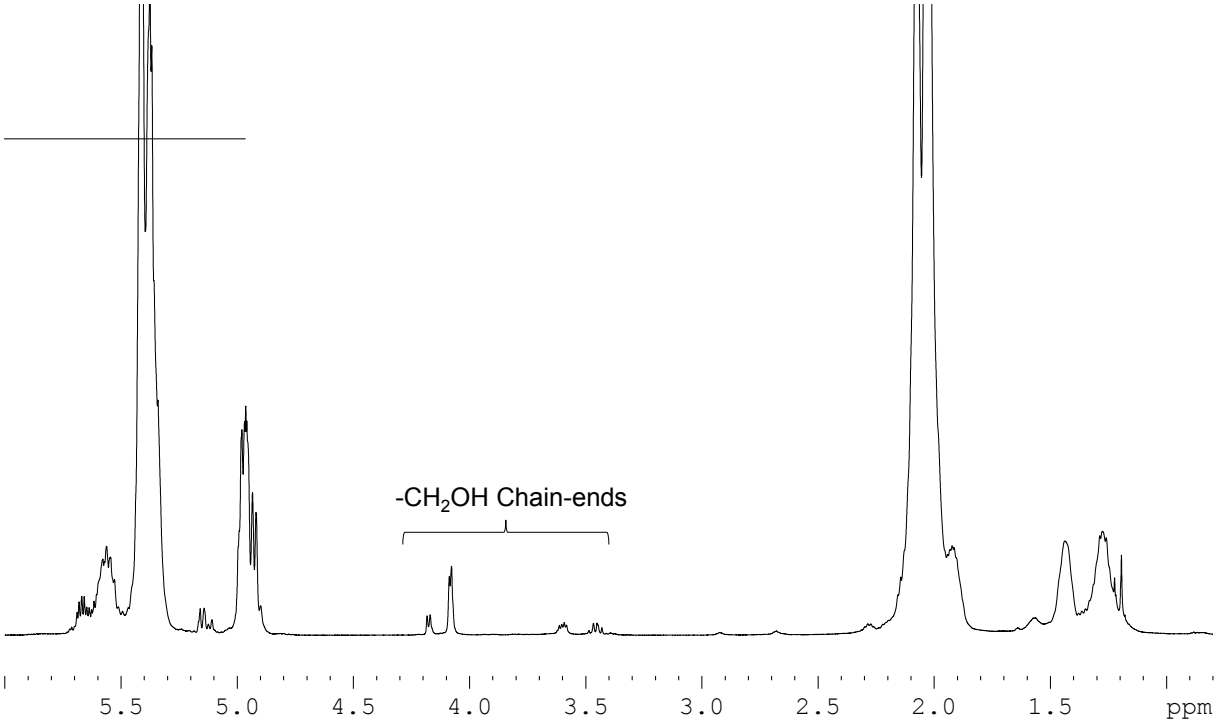

Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PBD-OH_2.

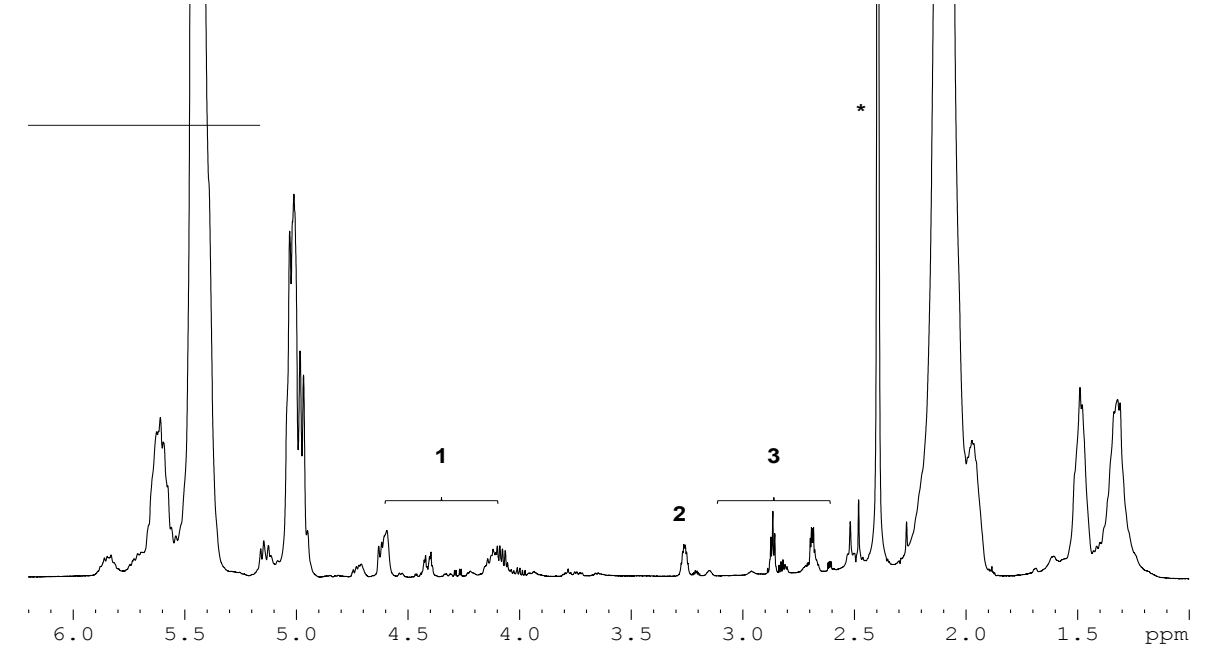

Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PBD-GC_2 (* marker stands for residual toluene).

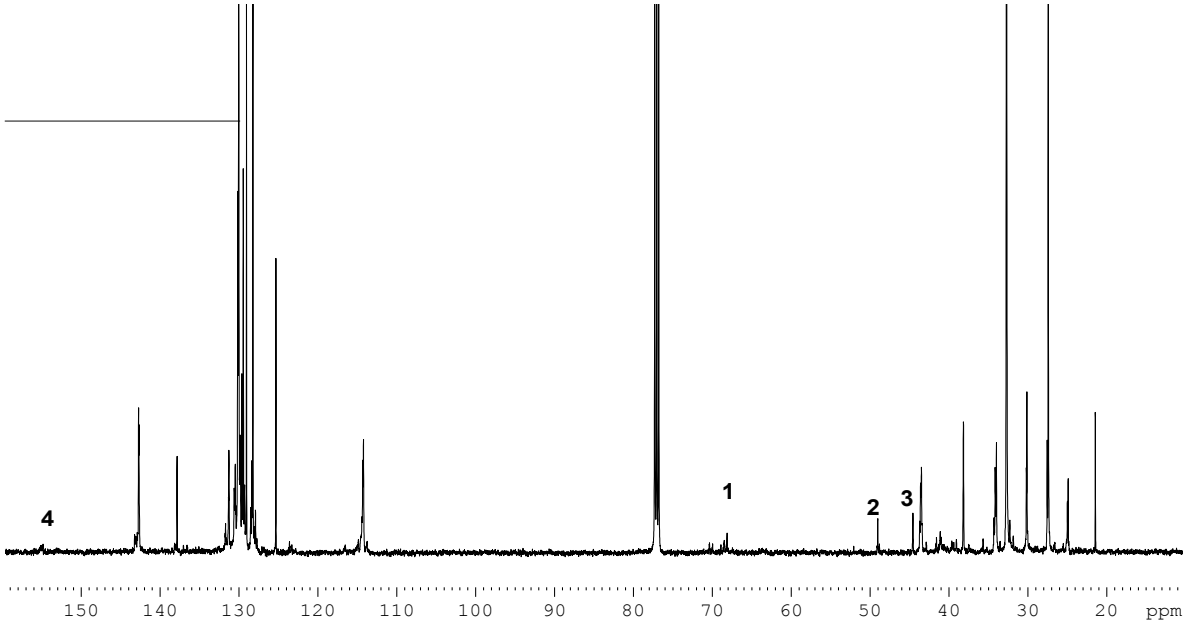

Figure S22. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 25 °C) spectrum of PBD-GC_2.

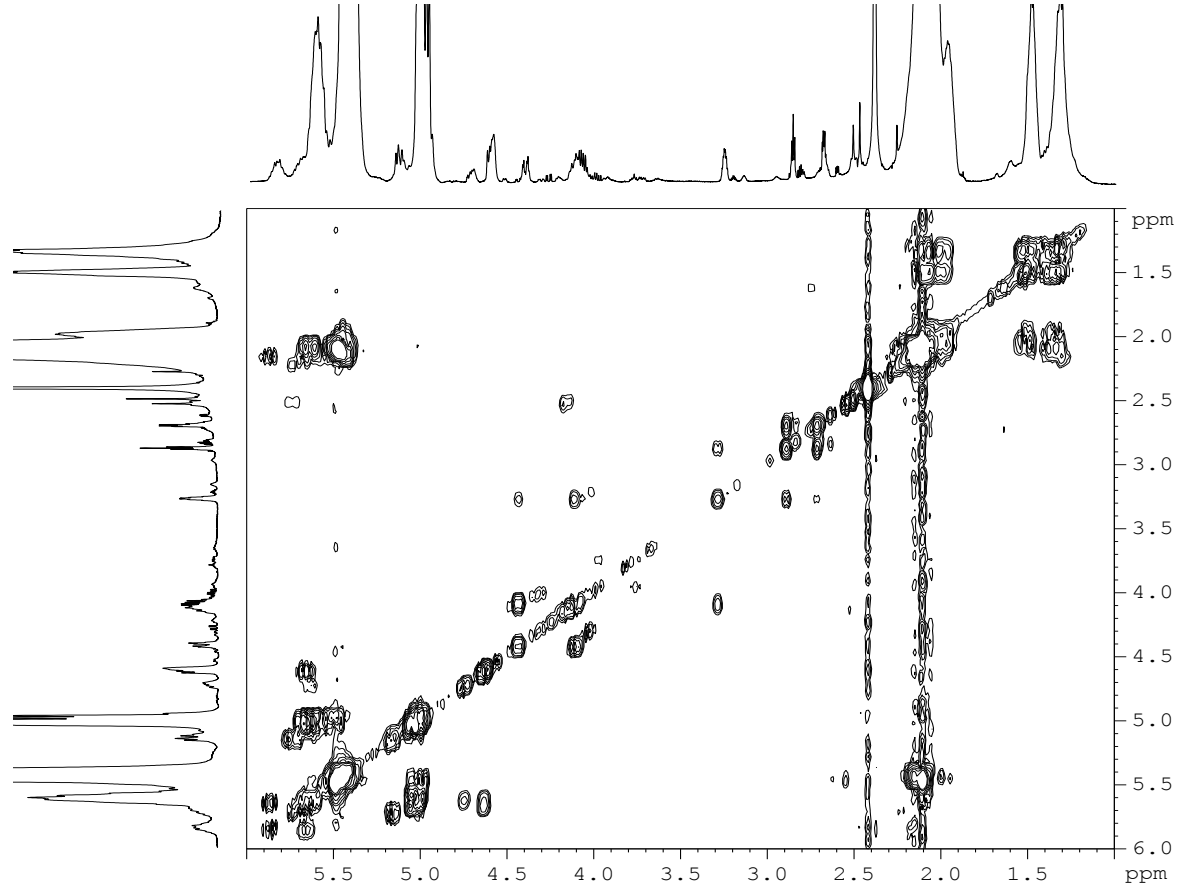

Figure S23. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of PBD-GC_2.

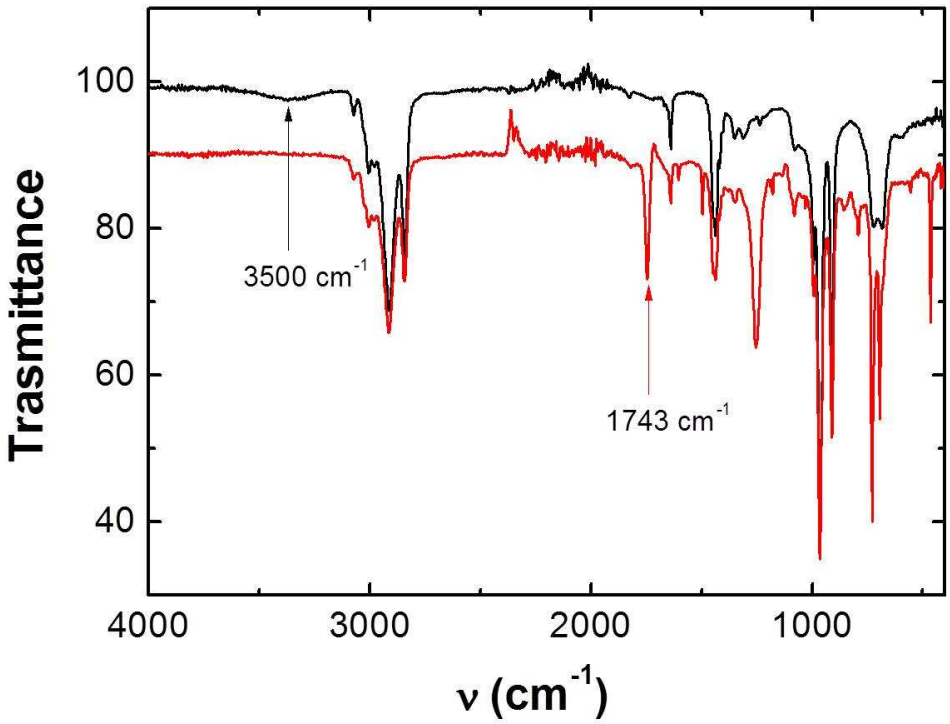

Figure S24. FTIR spectra of PBD-OH_2 (black trace) and the resulting PBD-GC_2 (red trace).

Scheme S1. Synthesis of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs).

Table S1. α,ω-Dihydroxy and dicyclocarbonate telechelic PEGs characteristics.

	$M_{n,SEC}$ [b]	$Đ_M$ [b]
PEG_{400}-OH_2	-	-
PEG_{400}-GC_2	-	-
PEG_{4000}-OH_2	3950	1.10
PEG_{4000}-GC_2	4400	1.18

[a] Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).

Table S2. α,ω-Dihydroxy and dicyclocarbonate telechelic PEE characteristics.

	$M_{n,NMR}$ [a]	$M_{n,SEC}$ [b]	$Đ_M$ [b]
PEE-OH_2	1000	1040	2.24
PEE-GC_2	1200	1090	2.14

[a] Determined by NMR analysis of the isolated polymer, from ^1H resonances of both terminal groups [b] Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).

Table S3. α,ω-Dihydroxy and dicyclocarbonate telechelic PBD characteristics.

	$M_{n,SEC}$ [a]	$Đ_M$ [a]	% 1,4-cis units	% 1,4-trans units	% 1,2 units
PBD-OH_2	3450	2.4	20.0	60.0	20.0
PBD-GC_2	3800	2.29	20.0	60.0	20.0

[a] Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).